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Journal of the Mineralogical Society of America

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THE AMERICAN MINERALOGIST

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Vol. 38 JULY-AUGUST 1953 Nos. 7 and 8

THE GENESIS OF PEGMATITES

I. OCCURRENCE AND ORIGIN OF GIANT CRYSTALS

RICHARD H. JAHNS, *California Institute of Technology, Pasadena, California*

ABSTRACT

Some masses of pegmatite contain individual crystals that are truly enormous in size, with dimensions measurable in feet or tens of feet, and weights that commonly amount to hundreds or even thousands of pounds. Such giant crystals are formed mainly by beryl, potash and sodaclase feldspars, quartz, spodumene, and the micas biotite, muscovite, and phlogopite, and to lesser extents by allanite, amblygonite, apatite, columbite-tantalite, fluorite, hornblende, hypersthene, monazite, petalite, median and calcic plagioclase, topaz, tourmaline, triphylite-lithiophilite, triplite, and other species.

Most of the giant crystals show rough external faces and are morphologically simple. Some are regular in form, whereas others are tapered or are marked by less systematic variations. Most of the crystals occur singly, but some others are grouped in irregular clusters, and many of those with prismatic or tabular habit form groups in which the individuals are parallel, radiating, or diversely oriented. A few species, notably quartz, beryl, and amblygonite, also occur as huge anhedral crystals.

Nearly all the giant crystals occur in pegmatite bodies that are zoned, i.e., that comprise lithologically distinctive units whose more or less concentric disposition within each body tends to reflect its shape and structure. In general the grain size of the zones in such a pegmatite body increases inward from its walls to its center, though not at a uniform rate. The giant crystals thus are most abundant in the interior parts of the body. They occur chiefly in rock with giant pegmatitic texture, which is characterized by extremely large, euhedral to anhedral crystals that are of nearly uniform size or tend to reflect a continuous variation in size.

The giant crystals show systematic trends in their distribution and size, and these trends are in full accord with all systematic trends and textural variations within the pegmatite body as a whole. Like the lithologic zones that contain them, they appear to have developed successively from the outer parts of a given pegmatite body inward toward its center. Many individual crystals of elongate habit plainly grew in the same general direction.

Convincing direct evidence that the giant crystals grew by replacement of other minerals appears to be lacking; instead, the excellent evidences of replacement that are widespread and clearly displayed in so many pegmatites apply to attack and replacement of the giant crystals by aggregates of younger, generally much finer-grained minerals. The problem of support during growth from a liquid, so often cited as an argument for a replacement origin of very large crystals, is readily resolved in most occurrences, where some type of effective support can be demonstrated. Several other features that are compatible with the replacement theory seem equally well explainable in terms of primary crystallization of the giant individuals from a solution.

Many investigators have concluded that pegmatite zones were formed by fractional crystallization of a magma, with incomplete reaction between successive crops of crystals and rest-liquid. The giant crystals in pegmatites are here considered to be primary constituents of these zones, mainly on the basis of their systematic distribution, age relations, textural and structural relations, and variations in composition. They are thought to have crystallized directly from pegmatite liquid that was rich in hyperfusible constituents, probably under restricted-system conditions involving rather delicate thermal and chemical balance.

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INTRODUCTION

The very coarse development of minerals in most masses of pegmatite makes this rock type a particularly inviting one for detailed examination and study. Even casual scrutiny, however, soon dispels any original impression of simplicity, but reveals instead many fine-grained constituents, as well as variations of structure, texture, or mineralogy that generally suggest a complex history of crystallization. Moreover, the interpretation of these features rarely is a simple matter, as demonstrated, for example, by the many conflicting opinions to be found in the extensive literature on pegmatite genesis.

The term pegmatite is applied by geologists mainly to those intrusive igneous rocks that are holocrystalline and at least in part very coarse grained. Marked irregularities in grain size are characteristic, and in some masses of pegmatite the coarsest crystals are enormous. The very size of such giant crystals is most provocative, and brings first to mind the oft-repeated question of just how large a crystal can grow. More than this, though, it provokes further thought as to what physical and chemical conditions are required for such spectacular nourishment of a relatively few crystal nuclei during the period of growth. And was this growth accomplished solely in a fluid environment, or was each new crystal lattice developed wholly or in part at the expense of pre-existing solid material? Before these and other questions can be approached effectively, however, the general features and relations of such giant crystals to the enclosing pegmatite must be known and, so far as possible, understood.

The writer's personal experience with giant crystals dates from a springtime day in 1932, when he spent several hours in collecting a well-faced 284-pound individual of potash feldspar from a mass of pegmatite in northwestern Riverside County, California. He clearly recollects his chagrin in discovering, a few weeks later, that this was by no means the largest known crystal of feldspar! In the years following, however, he had opportunity to observe and study many crystals of considerably greater size, and was especially fortunate in participating, during the period 1942–48, in an extensive program of pegmatite investigations by the U. S. Geological Survey. A specific study of exceptionally large crystals has been made since 1946, chiefly in the pegmatites of the Southwestern States; this work was supported by a research grant from the California Insitute of Technology.

The studies were greatly facilitated by Dr. D. F. Hewett of the U. S. Geological Survey, who supplied information on several pegmatite localities in southeastern California; by Mr. W. J. Alexander of the Whitehall Company, Inc., who introduced the writer to several areas of interesting pegmatite deposits in western Arizona; and by Dr. Arthur Montgomery of Lafayette College, who kindly furnished data and suggestions relating to results of his operations at the Harding mine in northern New Mexico. The writer also has profited from discussions in the field with Mr. L. A. Norman, Jr., of the California Division of Mines, and from later discussions, based on critical reviews of this manuscript, with his colleagues, Drs. Ian Campbell and A. E. J. Engel of the California Institute of Technology. Thanks also are due to Ellen Powleson, who drafted most of the sketches and diagrams, and to Florence Wiltse, who aided in the preparation of other parts of the manuscript.

SOME OUTSTANDING OCCURRENCES

Spodumene and the potash feldspars form the largest crystals thus far reported from masses of pegmatite, and particularly well known are the gigantic spodumene "logs" from the Black Hills region of South Dakota. Blake (4; 5, p. 608) long ago described a spodumene crystal 36 feet long and 1 to 3 feet thick from the Etta pegmatite; Hess (17, p. 651) and Ziegler (42, p. 654) later noted one that was 42 feet long and approximately 3 by 6 feet in section, and Schaller (34) described and pictured an immense crystal that was 47 feet in exposed length. Some-

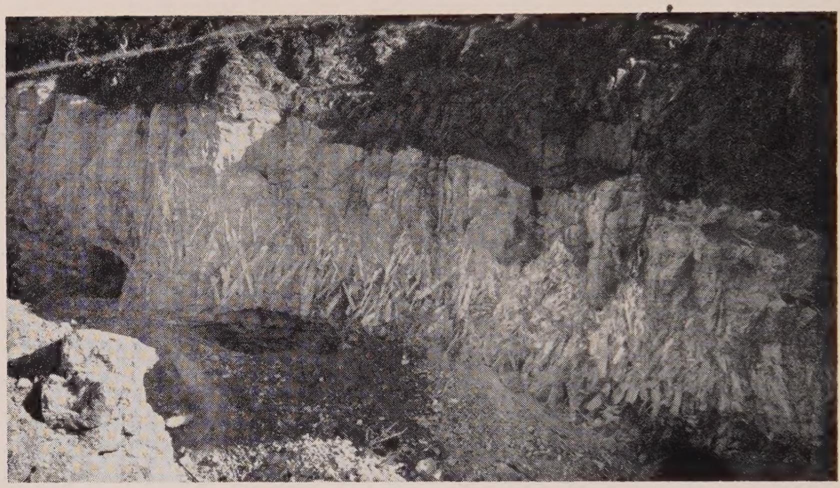

FIG. 1. Fringe-like aggregate of giant, lath-shaped spodumene crystals, Harding mine, New Mexico. The largest crystals are about 12 feet long. The quarry face here exposes the upper one-third of the thick, gently dipping pegmatite dike.

what smaller, though still giant, crystals of spodumene are present elsewhere in the Black Hills region, at several localities in eastern Manitoba, in the Kings Mountain region of North Carolina, in the Harding pegmatite of Taos County, New Mexico (Fig. 1; 8, Fig. 8), in a small area of pegmatites northeast of Wickenburg, Arizona, and in the Stewart pegmatite of San Diego County, California (24, Fig. 22). Similar occurrences have been reported from other parts of the world, and appear to be uncommon but by no means rare.

Giant crystals of perthite (mainly microcline with intergrowths of sodaclase feldspar) are more widespread in their occurrence, although fewer careful measurements seem to have been made of the largest ones. Most often quoted are the "individual feldspars more than 10 meters in length" that were noted by Brögger (6, p. 231) in pegmatite dikes south of Moss, in Norway. Olaf Andersen, in a letter to Hess (19, p. 455), mentioned a crystal 7 by 12 by 30 feet from the Iveland district, north of Kristiansand, and Lindgren (30, p. 754) noted that in the Ural Mountains of Russia a quarry was opened in a single orthoclase crystal! Bastin (2, p. 13), in his early report on feldspar deposits of the United States, mentioned single crystals 20 feet across, and a 20-foot crystal was described from the American mine, at Groton, New Hampshire, by Crosby and Fuller (10, pp. 154–155). Cleavage surfaces 20 to 23 feet across were observed by the writer in underground workings of the Coats and Kiawa mines, near Petaca, New Mexico, and crystals only slightly smaller are known from many other occurrences in the southwestern United States. Five- to 10-foot individuals are mentioned in published descriptions of pegmatites and pegmatite deposits too numerous to mention individually.

Well-faced crystals of pegmatite quartz, some of them a foot or more in diameter, have been recorded by Crosby and Fuller (10, p. 336), Kemp (26, p. 706), Frondel (13, p. 473), and many others, and Hess (18, p. 289) has remarked that "quartz crystals from a number of pegmatites have weighed more than 1,000 pounds each." Evidently overlooked by most observers, however, are the anhedral individuals of similar or even much greater size that form aggregates of so-called massive quartz, or "bull quartz." Such aggregates are conspicuous in the interior parts of many pegmatite bodies, and commonly contain anhedral crystals that weigh several tons. The writer has seen rhombohedral cleavage surfaces 2 to 9 feet across in the quartz cores of several large pegmatite masses in western Arizona and southern California, and such coarse textures are by no means rare in many other areas.

The micas, as represented by muscovite and phlogopite, can take their place among the real giants of pegmatite crystals. Well-known sources of very large crystals include the pegmatites of Brazil, Ceylon, India, Madagascar, Russia and Siberia, the Transvaal, eastern Canada, and the southeastern United States. Two of the most outstanding occurrences are at the Purdy mines in Mattawan Township, Ontario, from which Spence (38, p. 547) recorded a muscovite crystal 9½ feet by 7 feet in plan and nearly 3 feet thick, and at the Lacey mine in Loughborough Township, Ontario, whence Ellsworth (quoted in 32, p. 363) described an enormous crystal of phlogopite 14 feet in diameter and 33 feet long, with an estimated weight of "not less than 90 tons!"

Beryl, a widespread though not particularly abundant accessory constituent of many pegmatite bodies, forms some crystals of truly exceptional size. One of these was partly exposed for several years in the Ingersoll No. 1 pegmatite, in the Black Hills region of South Dakota; a gigantic hexagonal prism (39), it was measured at different times by Hess (18, p. 289), who reported a basal diameter of 45 inches, and by Connolly and O'Harra (9, p. 254), who reported the diameter of another section as 46 inches. Although its length never was determined accurately, this prism probably weighed more than 30 tons. A mass of beryl weighing approximately 100 tons is reported from the same pegmatite by Page,* who also notes a tapering prismatic crystal, once exposed in the Bob Ingersoll No. 2 mine, that was 18 feet long and 6 feet in maximum diameter. Another immense crystal, 18 feet long, 4 feet in diameter, and weighing about 18 tons, was noted from Albany, Maine, by Gedney and Berman (14, p. 79).

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* Page, L. R., Personal communication, 1952.

Several large "logs" of beryl were taken from partly kaolinized feldspathic pegmatite at the Herbb No. 2 mine, in Powhatan County, Virginia, during operations for sheet mica in 1944. This interesting occurrence has been described by Brown (7, p. 265). One of the crystals, as "reconstructed" by the writer from huge segments on the dump, must have been about 14 feet long and 17 to 23 inches in diameter. A somewhat different but no less spectacular occurrence was encountered at the Harding mine in northern New Mexico, where a 23-ton lens of beryl was mined in 1944 by Arthur Montgomery (31, p. 33). This irregular mass appeared to consist of several very large anhedral crystals.

Fluorite, a rather common accessory mineral in some pegmatite bodies, forms rudely faced crystals as much as 7 feet in diameter in several dikes of the Petaca district, New Mexico (Fig. 2; 21, p. 62). Dodecahedral crystals with somewhat smoother faces are scattered through the massive quartz of many dikes and pod-like masses of pegmatite northeast of Congress Junction, Arizona, where they reach diameters of 3 to 4 feet. Hess (16, p. 289) has reported crystals a foot across from the Baringer Hill, Texas, pegmatite.

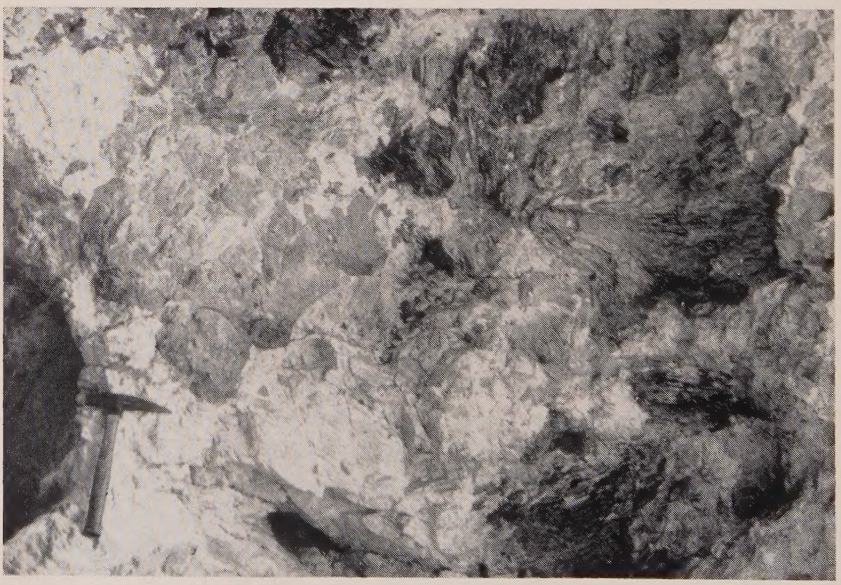

FIG. 2. Giant subhedral crystal of fluorite (dark gray, above hammer) in very coarse-grained quartz—perthite—muscovite—albite pegmatite, Globe mine, Petaca district, New Mexico. White albite veins and corrodes this crystal, as well as several large books of muscovite (upper right).

Rough crystals of amblygonite 4 to 5 feet in diameter are present in several pegmatite bodies near San Domingo Wash, northeast of Wickenburg, Arizona. Masses of amblygonite weighing tens of tons have been reported from the Black Hills region (18, p. 289), from the Stewart mine in San Diego County, California (24, p. 40), and from many other localities, but these appear to be very coarse-grained aggregates, rather than single giant crystals.

Other examples of unusually large crystals include the 9-foot prisms of black tourmaline that were exposed for many years in the walls of the Southern Pacific silica quarry near Nuevo, in Riverside County, California; strips of biotite 3 to 5½ feet long in several other southern California pegmatites; a book of biotite 6 feet wide, 9 feet long, and 2 feet thick reported by Andersen (19, p. 455) from a locality near Arendal, Norway; topaz crystals "up to 3 feet long" noted by Bandy (1, p. 521) from Portuguese East Africa; and a gigantic, smooth-faced, 596-pound topaz crystal, obtained from Minas Gerais, Brazil, that is now in the collection of the American Museum of Natural History. A columbite crystal, in part interleaved with several thin sheets of quartz, was reported from the Ingersoll No. 1 pegmatite in the Black Hills area by Blake (3, p. 341), who described it as 20 inches square, 24 inches long, and at least a ton in weight. A crystal of monazite, 6½ inches by 9½ inches by 11 inches in size, was described and pictured by Schaller (36, pp. 435-436) from a pegmatite deposit in Madison County, North Carolina. A 75-pound crystal of allanite was once collected by W. C. Brögger from pegmatite in Norway (26, pp. 707–708), and a mass of allanite weighing more than 300 pounds was reported from the Baringer Hill, Texas, pegmatite by Hess (16, p. 291).

This brief catalog of outstanding occurrences, though far from complete, should suffice as a background for more detailed consideration of the individual crystals. It is evident that many different mineral species form these unusually large individuals in pegmatite, and that such giant-textured pegmatite is widespread in its geographic distribution. No attempt will be made in this paper, however, to outline or to analyze the trends in geographic occurrence of various species of giant crystals. The principal aim of the following discussion is to summarize the characteristics of such crystals and the features of their occurrence within masses of pegmatite, and to consider these features in broad genetic terms.

General Features

Chief among the pegmatite minerals that form crystals of exceptional size are quartz, beryl, potash and sodaclase feldspars, spodumene, and the micas biotite, muscovite, and phlogopite. Such other minerals as amblygonite, apatite, fluorite, petalite, and tourmaline are less widespread, and among the rarer species should be listed allanite, columbite-tantalite, monazite, topaz, triphylite-lithiophilite, and triplite. Most of these minerals occur in pegmatite of granitic to monzonitic composition, but many also occur in quartzdioritic and granodioritic pegmatite. Hornblende, hypersthene, plagioclase, and a few other species are characteristic of very coarse-grained pegmatites that are more basic in composition, but in general do not form individuals of such great size as the minerals noted above.

The numerous examples of giant crystals already cited will give some idea of the maximum sizes that are attained. The dimensions of such individuals are measurable in feet or even in tens of feet, and their weights commonly amount to hundreds of pounds. Some of the largest individuals of beryl, feldspar, mica, and spodumene weigh many tons. In general, the ranges of size and weight vary considerably from one mineral species to another, and, for a given species, from one pegmatite body to another.

Most of the crystals show external faces, and ordinarily their form is typical for the species involved. Thus prismatic crystals are characteristic of most apatite, beryl, spodumene, and tourmaline, whereas crystals of amblygonite, fluorite, and monazite are stubby or equant. Some giant individuals of perthite are equant, but in other occurrences the crystals are much elongated parallel to the *a*-axis. The micas also show some variation in habit. Most characteristic are thick tablets, but a few crystals are greatly elongated parallel to their *c*-axis and form rough prisms, some of which taper markedly. Other crystals, notably of biotite, form thin strips and blades whose flat surfaces are parallel to the principal cleavage direction. Columbite and allanite generally occur as thick tablets and rough, nearly equidimensional masses, but long blades and prisms also have been observed.

Some of the individual crystals, particularly the largest ones of elongate habit, are distinguished by gross variations of form. Spodumene and tourmaline commonly taper from one end to the other, as traced along the *c*-axis of the crystal, and the perthite crystals in many pegmatite bodies show similar tapering along the *a*-axis. Tapered crystals of beryl are somewhat less common. Most of these show a progressive cross-sectional thinning along the *c*-axis from one end to the other, the remainder a thinning toward both ends from a central maximum. Less regular variations of form are known from crystals of both these and other mineral species.

Most of the giant anhedral crystals are equidimensional or nearly so.

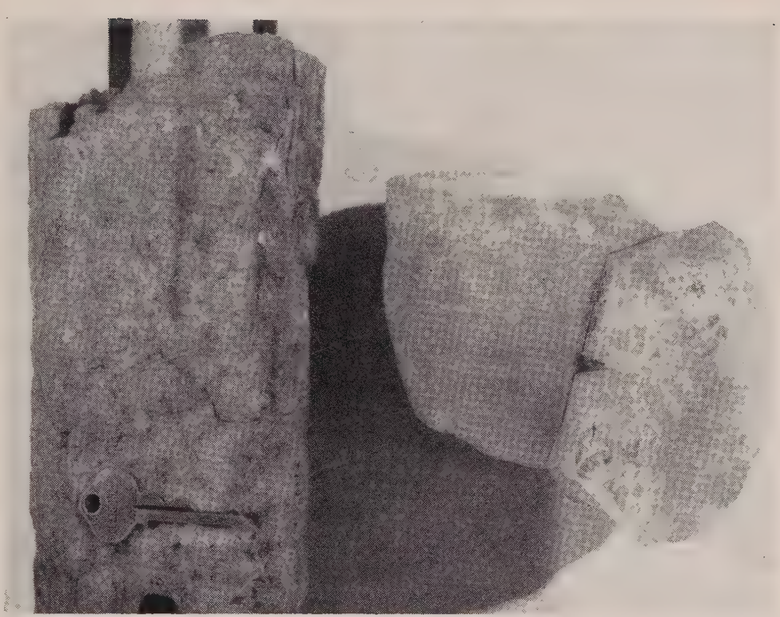

Fig. 3. Contrast in form and surfaces of crystals of pale blue beryl, San Pedro mine, Pala district, California. Large, rough prism at left is from very coarse-grained quartz—perthite pegmatite; stubby, smooth-faced, partly transparent prisms at right are from a pocket at the center of the same dike.

Quartz is most abundantly represented among such crystals, but this form also is developed by some beryl and several of the lithium-bearing phosphates. Nearly all the anhedral crystals have rough, highly irregular surfaces.

Those giant crystals that are euhedral tend to be morphologically simple, with development of a relatively few broad faces that are characteristically rough in detail. In marked contrast are the much more nearly perfect, mirror-like faces so commonly found on smaller, morphologically more complex crystals of the same mineral that occur elsewhere in the same pegmatite body (Fig. 3). Moreover, the giant crystals are nearly everywhere milky or opaque, whereas the smaller and more smoothly faced crystals typically are much more transparent.

Many of the giant crystals are single, separate individuals that are scattered through the enclosing pegmatite like plums in a pudding. Others, particularly those of elongate habit, form groups in which the individuals are parallel, radiating, or diversely oriented. Some of the spodumene "logs" in the Etta pegmatite of the Black Hills region form a mesh-like aggregate of gigantic, randomly disposed jackstraws, whereas others extend radially outward from masses of much finer-grained pegmatite, as pointed out by Hess (18, p. 295). Huge, lath-shaped crystals of the same mineral, where exposed in the gently dipping Harding dike of northern New Mexico, are arranged in a fringe-like aggregate whose principal elements are vertical or nearly so (Fig. 1). Most of the crystals are tapered, and have been described by Hess (18, p. 295) as "pointing upward." Similar arrangements are characteristic of much tourmaline, muscovite and other micas, and allanite, as well as some quartz and beryl. Preferred orientation of prismatic or tabular crystals generally occurs at or near the walls of a pegmatite body, and the crystals that are present in the more central parts of the body ordinarily show diverse attitudes.

Relations to the Pegmatite Framework

Nearly all the crystals of giant size occur in pegmatite bodies that are zoned, i.e., that comprise lithologically distinctive units that are more or less concentrically disposed within a given pegmatite body and reflect, at least to some degree, its general shape and structure (Fig. 4). These systematically arranged units have drawn the attention and comments of pegmatite investigators for many years, and recently were described, classified, and discussed in considerable detail by Cameron, Jahns, McNair, and Page (8, pp. 11-70). As recognized from the walls of a given pegmatite body inward toward its center, these units have been termed border zone, wall zone, intermediate zone (or zones), and core. In general, the coarsest minerals occur in cores and intermediate zones (Fig. 4), but the wall zones of some pegmatite bodies also contain giant crystals.

Ordinarily there is some correlation between the size of a pegmatite body and the size of giant crystals within it, and Cameron, et al. (8, p. 59) have noted, for example, that "the larger the body in question the larger the crystals in the core." Most of the giant crystals cited in the first part of this paper occur in pegmatite bodies with minimum dimensions of at least several tens of feet, and in general are present only in certain parts of these bodies. The correlation of sizes is only a rough one, however, and it cannot be applied to all occurrences. Thus many very large pegmatite bodies contain no giant crystals, and, in contrast, some fairly small bodies do contain such crystals. Outstanding examples of the latter are several dikes at the Purdy mine in Ontario, in which enormous books of muscovite extend nearly from wall to wall.

Of particular significance in the sequence of lithologic units within a zoned pegmatite body is a characteristic sequence of textures. By far the most widely represented are granitoid, prophyritic, and giant peg-

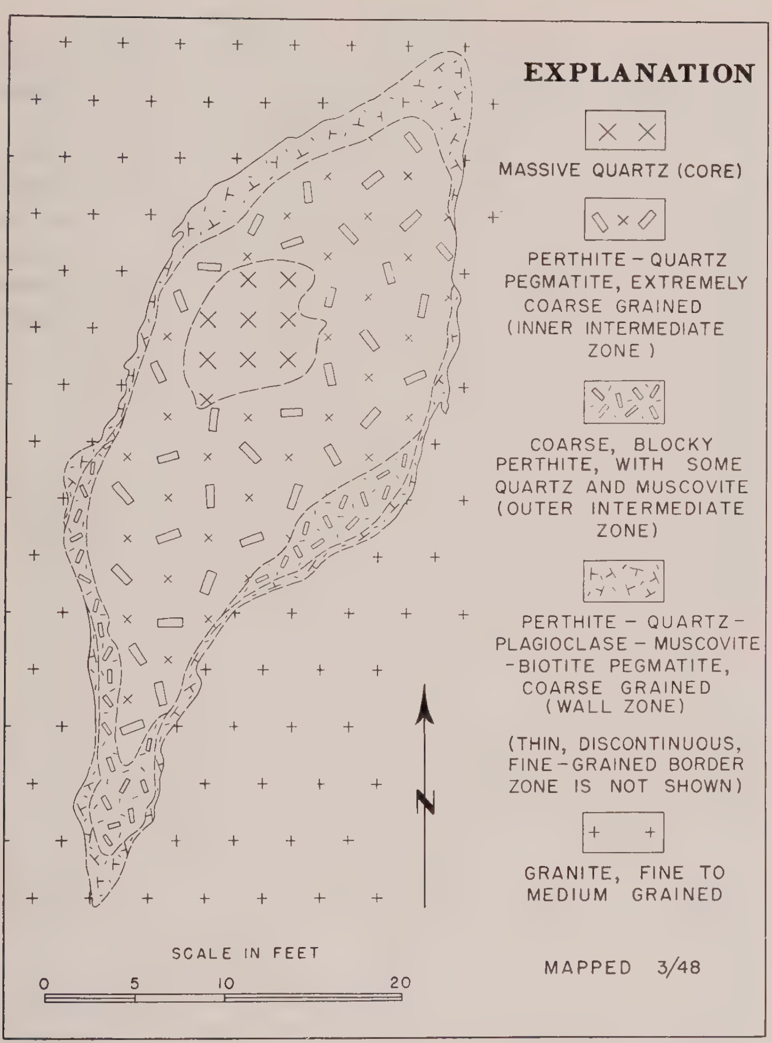
EXPLANATION
MASSIVE QUARTZ (CORE)
PERTHITE – QUARTZ PEGMATITE, EXTREMELY COARSE GRAINED (INNER INTERMEDIATE ZONE)
COARSE, BLOCKY PERTHITE, WITH SOME QUARTZ AND MUSCOVITE (OUTER INTERMEDIATE ZONE)
PERTHITE – QUARTZ – PLAGIOCLASE – MUSCOVITE – BIOTITE PEGMATITE, COARSE GRAINED (WALL ZONE)
(THIN, DISCONTINUOUS, FINE-GRAINED BORDER ZONE IS NOT SHOWN)
GRANITE, FINE TO MEDIUM GRAINED
N
SCALE IN FEET
0
5
10
20
MAPPED 3/48

FIG. 4. Geologic map of a small, pod-like pegmatite body, showing typical concentric arrangement of zones. Relative coarseness of the pegmatite units is indicated diagrammatically by the map patterns. Robbins silica prospect, San Bernardino County, California.

matitic textures, which generally appear in this order from the walls of a pegmatite body inward to its center.

Granitoid, as used in the standard sense of the term, refers to pegmatite in which the mineral grains are dominantly anhedral and approximately the same size (Fig. 5). In nearly all granitoid pegmatite they are 8 inches

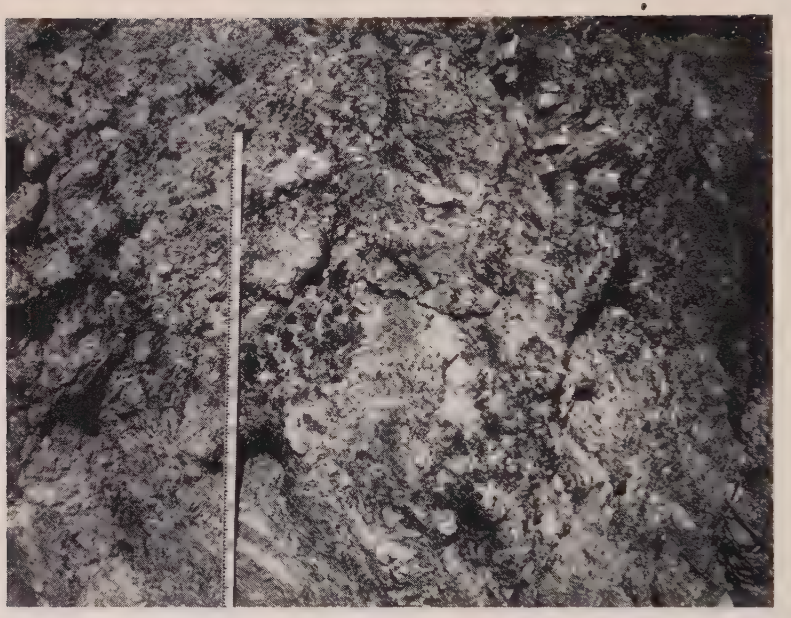

FIG. 5. Coarse-grained perthite—quartz—muscovite—albite pegmatite, Joseph mine, Ojo Caliente district, New Mexico. The texture of this rock is granitoid in the vicinity of the stadia rod, but several very large masses of perthite and quartz appear in the right-hand part of the exposure.

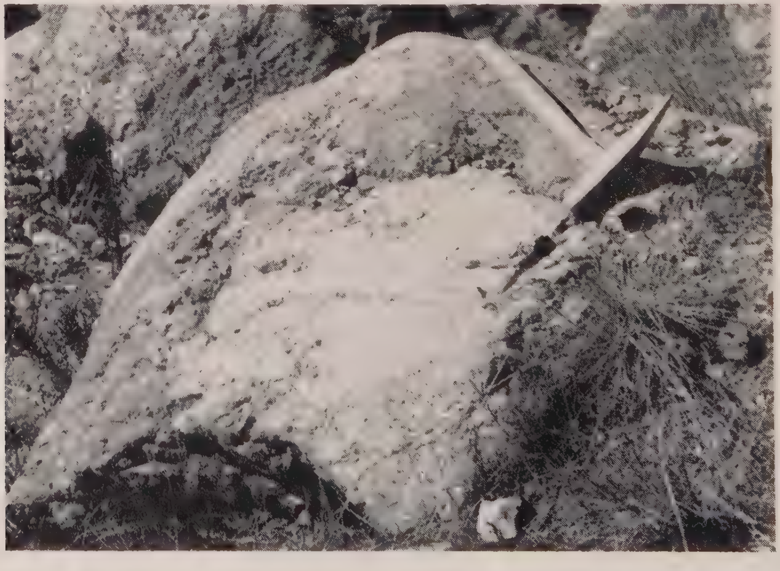

FIG. 6. Porphyritic perthite—plagioclase—quartz—muscovite pegmatite, Senpe mine, Pala district, California. In foreground light is reflected from large, ragged phenocryst of perthite, which contains much graphically intergrown quartz.

or less in maximum dimension. Departures from the normal texture are caused mainly by the tendency of some minerals, notably the micas, to develop crude crystal faces, and by the occurrence in some pegmatite of scattered crystals that are larger than the others. No such crystals reach giant size, however.

Porphyritic texture, as typically developed in pegmatite, results from the occurrence of very large, prominent crystals, or phenocrysts, in a groundmass of distinctly smaller crystals (Fig. 6). The phenocrysts are subhedral or euhedral, with very rough and irregular faces, and most are 1 to 4 feet in maximum dimension. The most abundant phenocryst constituent is perthite, with or without graphically intergrown quartz. Apatite, beryl, garnet, and tourmaline also occur as very large crystals in some varieties of porphyritic pegmatite. The beryl crystals commonly are anhedral, in contrast to the phenocrysts of the other minerals.

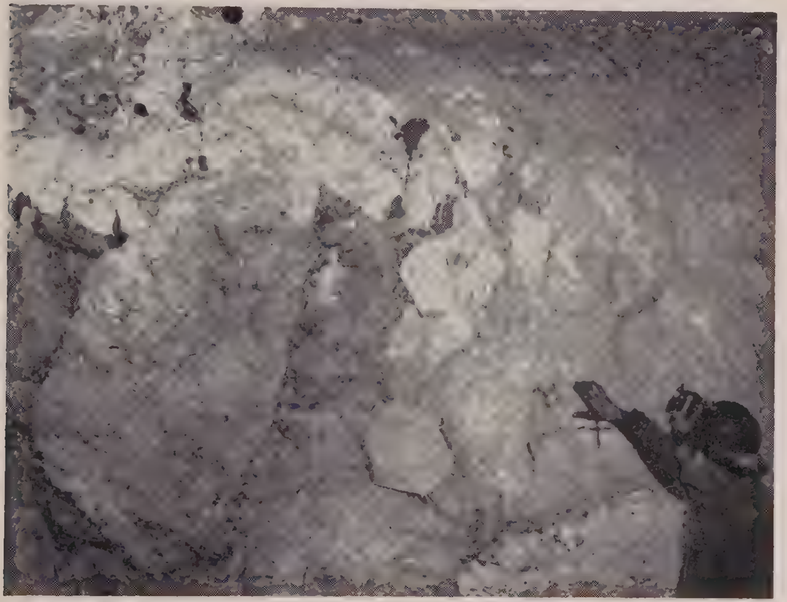

FIG. 7. Exposure showing giant pegmatitic texture, Cribbenville mine, Petaca district, New Mexico. The giant, subhedral crystals of perthite are not phenocrysts, as the enclosing quartz (dark gray) is equally coarse grained. The large, white masses at the upper left and lower right are cleavelandite, in which are scattered books of muscovite (very dark gray).

Giant pegmatitic texture, as herein applied to the coarsest parts of many pegmatite bodies, is characterized by extremely large, euhedral to anhedral crystals that are of nearly uniform size or show a more or less continuous variation in size (Fig. 7). Such pegmatite is therefore

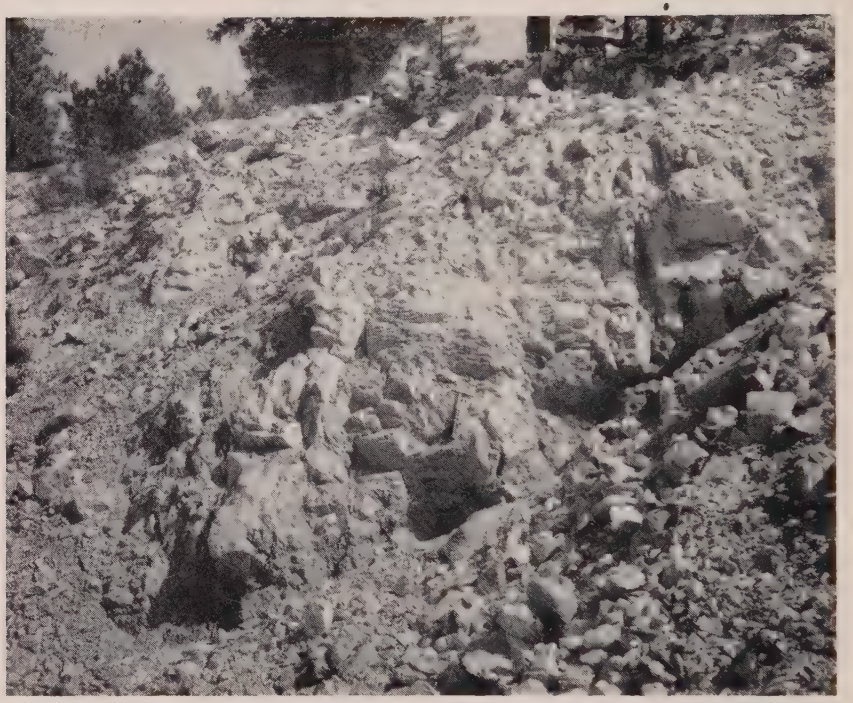

FIG. 8. Typical massive quartz in the central part of a pegmatite body, Kiawa mine, Petaca district, New Mexico. The quartz forms anhedral crystals that are 1 foot to 8 feet in diameter, and hence the rock is much coarser grained than it appears to be. Note the many closely spaced fractures.

non-porphyritic, though not necessarily even grained. Pecora, et al. (33, p. 250) have aptly designated this texture in Brazilian pegmatites as "a gigantesque variation of the granitic pattern." The terms pegmatitic and micropegmatitic have been applied by some authors to certain geometrically regular intergrowths of minerals, but such alternate terms as graphic, micrographic, and granophyric seem more appropriate in this connection. These intergrowths are relatively fine grained, and hence texturally quite distinct from giant pegmatitic aggregates, which contain most of the largest crystals to be found in pegmatites.

Giant pegmatitic textures are most commonly developed in zones of massive quartz (giant anhedral crystals) (Fig. 8), quartz-perthite pegmatite (Fig. 7), quartz-spodumene pegmatite (Figs. 1, 10), and quartz-perthite-tourmaline pegmatite. The mineralogy of these extremely coarse-grained rock units ordinarily is very simple, and rarely are more than three species represented among the large crystals of a given unit.

Other kinds of texture are present in many masses of pegmatite, but

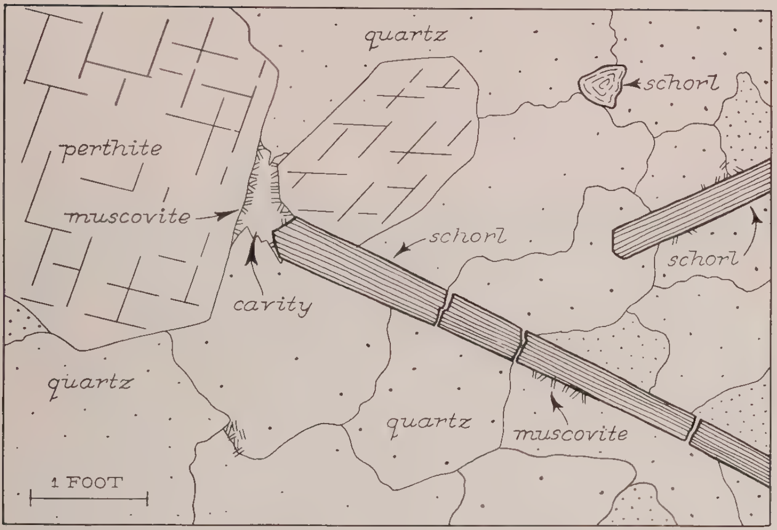

FIG. 9. Giant pegmatitic texture in quartz—perthite—schorl core of large pegmatite dike near Sage, Riverside County, California. The large crystals show smooth faces where they form the walls of the small cavity. Contacts between anhedral quartz crystals are diagrammatic, but positions of most are correct to within an inch.

are subordinate to the three principal types described above. Graphic intergrowths, chiefly of quartz in potash feldspar (graphic granite), are widespread, and the host crystals commonly are phenocrysts in porphyritic varieties of pegmatite (Fig. 6), or occur in varieties with giant pegmatitic texture. Some pegmatite shows miarolitic texture, and contains irregular cavities or pockets that are walled with well-faced crystals. Most of these cavities occur in the very coarse-grained central parts of zoned pegmatite bodies, but some others, generally smaller ones, lie in the outer parts. Crystals of considerable size are present in some cavities, but rarely are they as large as other crystals of the same minerals that occur in nearly solid rock. These other crystals generally lie entirely outside the cavities, but a few terminate as parts of the cavity walls (Fig. 9).

Textural complexities are characteristic of pegmatite bodies that contain fracture fillings or masses of replacement material. Thus giant crystals of one mineral commonly show fracturing and subsequent healing by another mineral (Fig. 10), or are veined and corroded by aggregates of much finer-grained material (Figs. 2, 11). All degrees of replacement can be observed in some giant crystals, ranging from thin, fracture-controlled stringers to stockworks or widespread disseminations of the younger material in the older. Common end-stage products are huge pseudomorphs and partial pseudomorphs of sugary albite after perthite, albite after muscovite, muscovite or hydrous mica and clay minerals after spodumene, fine-grained muscovite after topaz, fine-grained muscovite and clay minerals after tourmaline, and hureaulite after lithiophilite, to name only a few. These and other products of fracture-filling and replacement processes have received much attention in the literature on pegmatites, and recently have been summarized and discussed by Cameron, et al. (8, pp. 70–97).

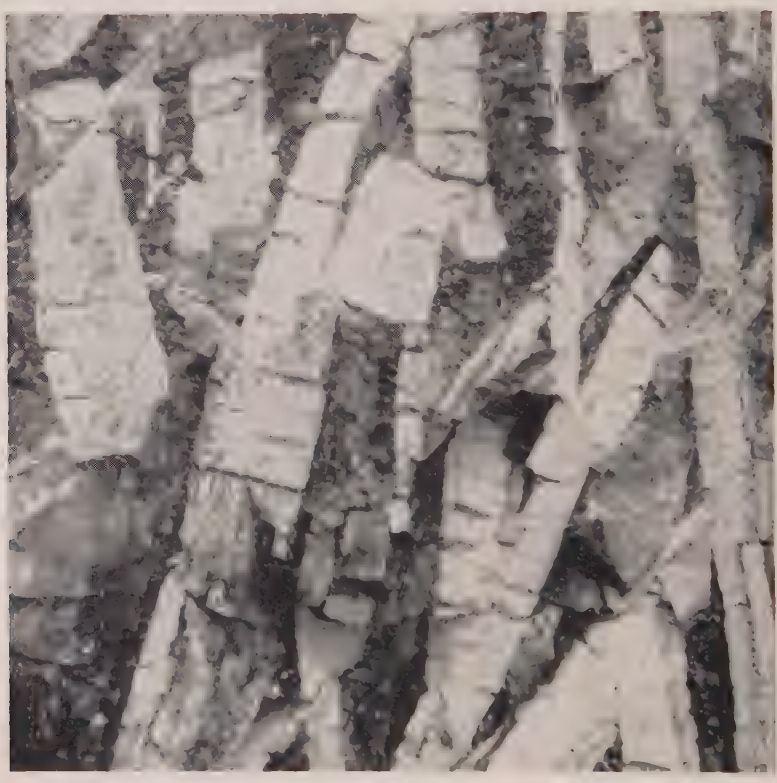

Fig. 10. Detail of giant laths of spodumene showing "healed-fracture" structure, Harding mine, New Mexico. Note matching walls of fractures, which are filled with gray quartz like that enclosing the laths. Width of largest spodumene crystals is about 10 inches.

In general the grain size of a pegmatite body that contains giant crystals increases from its walls to its center, or from its border zone to its core. As shown in Fig. 12, the rate of increase is far from uniform. In most occurrences the average grain size increases gradually inward from the walls, thence very markedly and abruptly, and thence very slightly into the core. In some pegmatite bodies, especially very large ones, there is a slight decrease at the center, and in those pegmatite bodies with cavities or much replacement material there is a considerable final decrease.

The narrow region of marked increase in grain size reflects the generally sharp boundary between granitoid or porphyritic pegmatite, on the one hand, and the giant pegmatitic aggregate that forms the interior part of the mass, on the other. If a plot of grain size is made on the basis of the largest crystals, rather than the average crystals, the major break in the curve is moved to the left and softened somewhat (Fig. 12), particularly for those pegmatite bodies that contain a porphyritic zone.

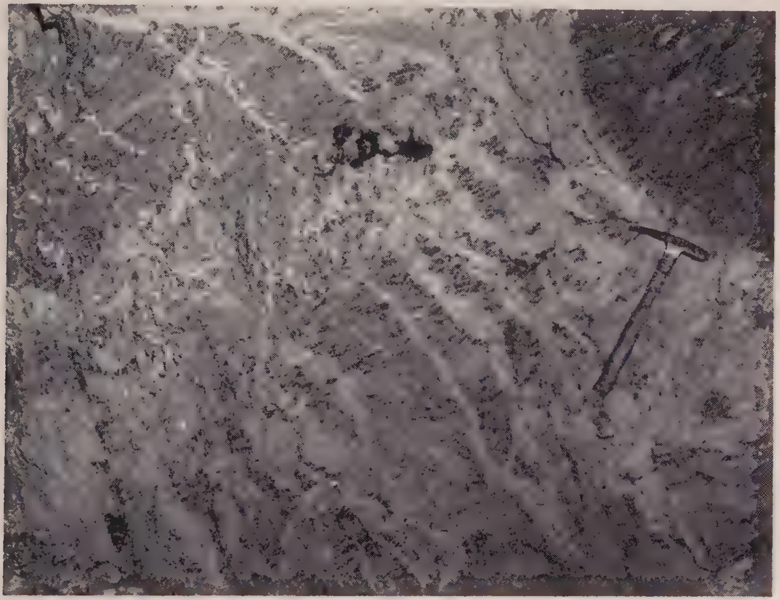

FIG. 11. Gigantic crystal of perthite (dark gray), veined with cleavelandite and encroached upon by fine-grained aggregates of quartz, albite, and muscovite. Globe mine, Petaca district, New Mexico.

The curves shown in Fig. 12 are derived from the pegmatites of only one region, but in general shape they are applicable to most other pegmatites that contain giant crystals. Indeed, the abrupt increase in grain size is one of the most characteristic features of such pegmatite bodies. It occurs nearer the walls of some, nearer the centers of others, but invariably it can be correlated with a marked change in the rock fabric, involving especially the strong tendency of certain minerals to develop crystal faces. There is an accompanying tendency, at least in some pegmatites, toward a much simpler mineralogy immediately inside this textural break.

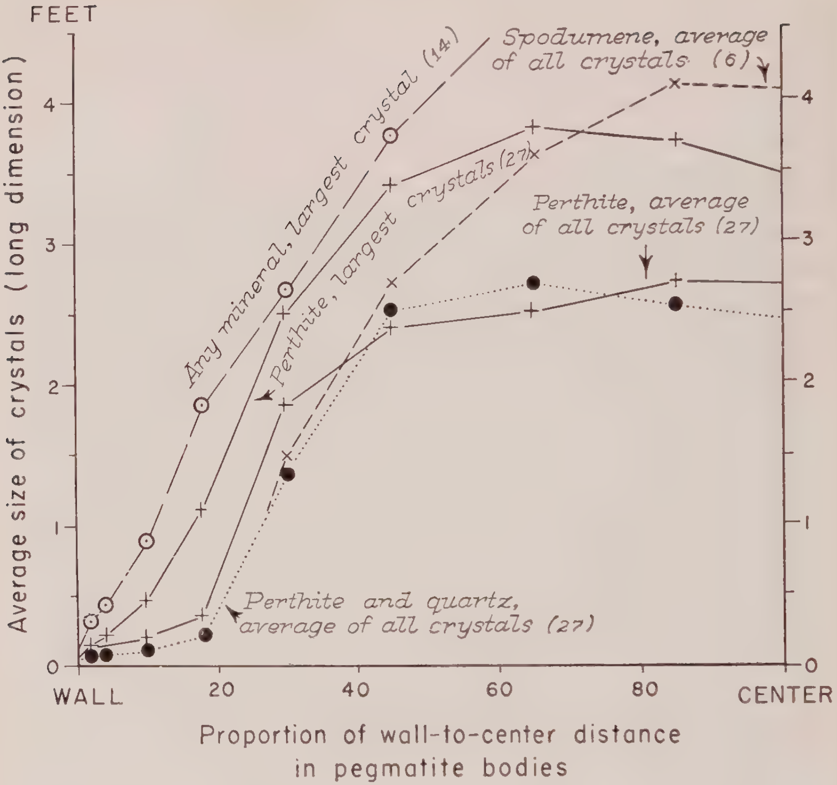

FIG. 12. Curves showing some general grain-size variations in large, zoned pegmatite bodies in the Hualapai, Bagdad, and White Picacho districts of western Arizona. Each curve represents an average of measurements made on the number of pegmatite bodies shown in parentheses; none of these bodies is less than 40 feet in maximum outcrop breadth. Each point on the "any mineral" curve represents an average that may involve more than one mineral species.

ORIGIN OF THE PEGMATITE FRAMEWORK

The crystallization of pegmatite minerals has been discussed by several generations of investigators, and various theories of genesis have been advanced to account for the characteristic structural, textural, and compositional features of pegmatite bodies. Excellent summaries of these theories have been provided by Kemp (26), Johannsen (25, pp. 74–84), and Landes (29, pp. 41–56), and the subject needs no detailed review here. The origin of zoned pegmatite bodies has been most recently discussed by Cameron, et al. (8, pp. 97–106) and by Flawn (12, pp. 180–190), who reached the conclusion that these rocks are mainly the products of primary crystallization from a magma, under restricted-system conditions (i.e., conditions approaching those of a closed system). The zonal structure has been attributed to fractional crystallization and incomplete reaction between successive crops of crystals and rest-liquid. This view thus reflects, wholly or in large part, the earlier conclusions of Brögger (16, p. 230), Crosby and Fuller (10, p. 157), Warren and Palache (40, p. 146), Kemp (26, pp. 708–709, 722), Landes (29, pp. 53–55), and Shaub (37, pp. 684–688).

It is not the primary purpose of this paper to present in detail the arguments for an essentially magmatic, or "closed-system," origin of the minerals indigenous to pegmatite zones. In summary, however, this concept rests mainly, in the present writer's opinion, upon combinations of eight major features of occurrence:

1. Widespread structural evidence for emplacement of original pegmatite fluid by mechanical injection, in many instances accompanied by digestion of country rock.
2. Consistent evidence for a sequence of zone development from the walls of a pegmatite body inward to its center.
3. Remarkable detailed correspondence in sequences of mineral assemblages from one zoned pegmatite to another.
4. Correspondence between the sequence of essential-mineral development in zoned pegmatites with the sequence of the same mineral species in normal igneous rocks; the sequence of major minerals in zoned pegmatites is basically that of Bowen's reaction series.
5. Similarities of pegmatite fabrics to those of many normal igneous rocks, despite the marked differences in grain size.
6. Strong concentrations of rare elements in some masses of pegmatite.
7. General accordance, in occurrences thus far investigated, between quantitative distribution of rare elements within zoned pegmatites and the distribution predicted for such elements on theoretical grounds.
8. Lack of field evidence that zones in a given pegmatite body were developed by successive replacement of pre-existing rock.

All known features of pegmatite zones seem reasonably explainable on the basis of crystallization from a melt of low viscosity, with or without end-stage deuteric or hydrothermal activity. Many of these features also suggest that masses of pegmatite crystallized inward from the walls of an original chamber, under restricted-system conditions, rather than in some sort of channelway or thoroughfare under more open-system conditions. The pod-like form and concentric internal structure of many pegmatite bodies support this general concept.

Most geologists view the fluid that forms zoned pegmatite bodies as a silicate rest-liquid derived by differentiation during the end stages of crystallization of ordinary plutonic or hypabyssal igenous rocks. Such a fluid also could be drived directly or by differentiation from a palingenetic magma formed through melting of pre-existing rocks, or possibly might be a product of granitization processes. Many investigators, however, have raised serious objections to granitization as a means of accounting for zoned pegmatites. It cannot be denied that much pegmatite may well have been formed from pre-existing rocks through processes of replacement, *in situ*, by highly attenuated fluids, but the rocks that appear to be products of such pegmatitization do not contain giant crystals, nor are they characterized by the internal zoning described above. Pegmatites of this type therefore are not considered in this paper.

The discussion has centered thus far about pegmatite zones and the minerals indigenous to these zones, with little mention of those minerals that plainly were developed by replacement of earlier pegmatite minerals. There is considerable argument among geologists—even among those who agree that pegmatite zones were formed by fractional crystallization from a liquid -regarding the relative importance of replacement processes, especially during the latest stages of pegmatite formation. The general concept of a magmatic stage and one or more hydrothermal stages in the development of the so-called complex pegmatite, as so clearly outlined by Landes (29, pp. 44–56), is variously applied by different investigators. In particular, arguments center about the proportion of replacement material in a given mass of pegmatite, and as to whether the replacing fluids were of deuteric origin (i.e., did the pegmatite body "stew in its own juice" under restricted-system conditions?) or were hydrothermal solutions derived from sources outside the pegmatite body. These questions are significant in terms of the origin of giant crystals in pegmatite.

ORIGIN OF THE GIANT CRYSTALS

The case for primary crystallization

Crystals of giant size have impressed many investigators as primary constituents of pegmatite zones, and hence as products of normal crystallization from a melt, magma, or other fluid. One of the principal reasons for this view is the consistency, from one pegmatite body to another, of the textural relations between the giant crystals and the framework of the pegmatite body in which they occur. These, moreover, are the relations that are typical of many masses of non-pegmatitic igneous rocks.

A given crystal of giant size ordinarily is larger than other crystals of the same mineral that lie nearer to the walls of the pegmatite body, and is about the same size or somewhat larger than those nearer the center of the body. Thus its size and position are fully compatible with the general textural relations within zoned masses of pegmatite, which show either a progressive inward coarsening to a maximum value at the center, or an inward coarsening to a maximum value, followed by some decrease in average grain size near the center. Interestingly enough, this last relation has been reported from many thick igneous dikes of non-pegmatitic rock, and has been interpreted for basaltic dikes by Winkler (41, pp. 562–574) in terms of magmatic crystallization. Naturally, however, Winkler's conclusions can be extended to zoned pegmatite bodies only in those occurrences where essentially closed-system conditions of formation can be established for the entire crystallization history of the pegmatite minerals involved.

Despite the impressive size of the typical giant crystal, it generally is surrounded by other crystals of comparable size, and hence is merely a part of a mineral aggregate with giant pegmatitic texture. This important feature is commonly overlooked, mainly because so many of the enormous crystals of perthite, spodumene, and other minerals occur in massive quartz, which comprises anhedral crystals whose own great size rarely is evident on casual inspection (Figs. 7, 8). Moreover, the quartz is shattered or partly granulated in the interior parts of many pegmatite bodies, which tends to obscure further its giant texture.

Some disparity in dimensions does exist, of course, between adjacent crystals of different mineral species, but this is common in most igneous rocks. Only in some very coarse-grained pegmatite with porphyritic texture is there a marked size difference between the giant crystal and its neighbors (Fig. 6), and here all significant textural relations at the crystal boundaries show plainly and consistently that the giant crystal developed first. This also is compatible with textural relations in more "normal" porphyritic igenous rocks with a much smaller general grain size, and may well reflect some departure from strictly closed-system conditions of formation.

Also meaningful is the consistent relation, in terms of composition and sequence of development, of giant crystals to the zonal structure of the containing pegmatite body. This is a reflection of the impressive consistency of mineral assemblages described in detail for zoned pegmatites by Cameron, et al. (8, pp. 59–70). The quartz-euhedral perthite zone of a given pegmatite body, for example, occurs nearer the walls than a quartz-spodumene zone in the same body, regardless of whether the perthite individuals are 6 inches or 6 feet in maximum dimension. The absolute size of the crystals is significant, to be sure, but is incidental to their relative size and to their sequence of development, and hence to their relative positions within the pegmatite body.

Well-defined trends in composition of mineral species can be recognized in many pegmatite bodies. Within such bodies, for example, the alkali content of the beryl, the lithium content of tourmaline and micas, the tantalum content and manganese-iron ratio in columbite-tantalite, and the proportion of albite in plagioclase commonly increase inward from the walls to the centers. These systematic variations seem most readily explainable in terms of fractional crystallization of pegmatitic liquid. The giant crystals reflect faithfully these trends, so far as their composition has been checked against that of other crystals of the same mineral species in the same pegmatite body.

The orientation of some huge crystals plainly indicates their inward growth from the walls of the containing pegmatite body. In describing spodumene crystals in contact with the outer, fine-grained part of the Silverleaf pegmatite in eastern Manitoba, Derry (11, p. 465) stated that they "increase in size away from the contact and those nearest to it are arranged with their long axes normal to the contact." A similar arrangement characterizes the spodumene laths near the walls of many pegmatite dikes in the Piedmont region of North Carolina, and Hess (20, pp. 954–956) has described and pictured some excellent examples. The fringing, or comb-like, arrangement of tapering spodumene crystals in the hanging-wall part of the Harding dike, in northern New Mexico, has been noted in a previous paragraph (Fig. 1). Tapering crystals of spodumene, tourmaline, perthite, and other elongate minerals are oriented perpendicular or nearly perpendicular to wall-rock contacts or to contacts between zones in many other pegmatite bodies.

Such crystals evidently began to develop from their pointed or thinner ends, and were progressively thickened as they extended inward toward the center of the pegmatite body. This direction of growth is indicated by the well-formed crystal faces at their thick ends, by some tendency toward a radiating, or stellate, arrangement of the crystals from their thin ends, and, perhaps most convincingly, by the disposition of "growth surfaces" within the crystals themselves. Excellent examples of such surfaces are present in elongate crystals of perthite in many pegmatite dikes of southern California. As described from the Mesa Grande district by Jahns and Hanley (23), these crystals are elongate, generally parallel to the *a*-axis, and taper rather uniformly from one end to the other. Their thin ends commonly lie at or near a wall of the enclosing dike, with their long axes perpendicular to the wall or nearly so. Many of these crystals contain phantoms, each of which is surfaced wholly or in part with a very thin, dust-like aggregate of mica flakes, schorl needles, or tiny crystals of salmon-pink garnet. The "dusted" surfaces mark successive stages in the growth of the perthite crystals (Fig. 13),

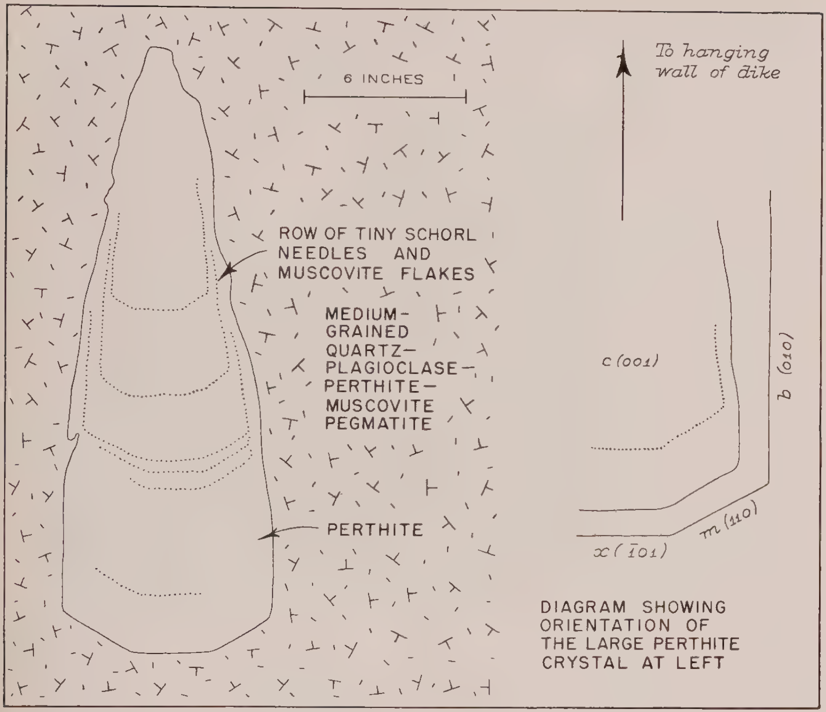
6 INCHES
ROW OF TINY SCHORL NEEDLES AND MUSCOVITE FLAKES
MEDIUM-GRAINED QUARTZ-PLAGIOCLASE-PERTHITE-MUSCOVITE PEGMATITE
PERTHITE
To hanging wall of dike
c (001)
b (010)
m (110)
x (1̄01)
DIAGRAM SHOWING ORIENTATION OF THE LARGE PERTHITE CRYSTAL AT LEFT

Fig. 13. Wedge-shaped crystal of perthite showing incomplete "phantoms," Mack mine, Rincon district, California. Crystal is elongate parallel to the a-axis, which is nearly normal to the hanging wall of the pegmatite dike.

and some are so continuously developed that well-faced phantom crystals are easily obtained by rough cobbing with a hammer. Similar phantoms (Fig. 14) are abundant in other pegmatite districts, both in southern California and elsewhere.

Finally, there seems to be a lack of direct evidence that the giant crystals grew by replacement of other minerals; indeed, most of their textural relations in the enclosing pegmatite indicate early development as phenocrysts, or essentially simultaneous crystallization with respect to immediately adjacent coarse-grained minerals. In other words, the giant crystals appear to be truly indigenous to the pegmatite zones in which they occur.

Fracture-fillings, as well as corrosion veins, pseudomorphs, and other replacement features are abundant and widespread in pegmatites, but these demonstrate attack and replacement *of the giant crystals*, generally yielding aggregates of younger, much finer-grained minerals. Examples of such replacement have been carefully described and discussed by

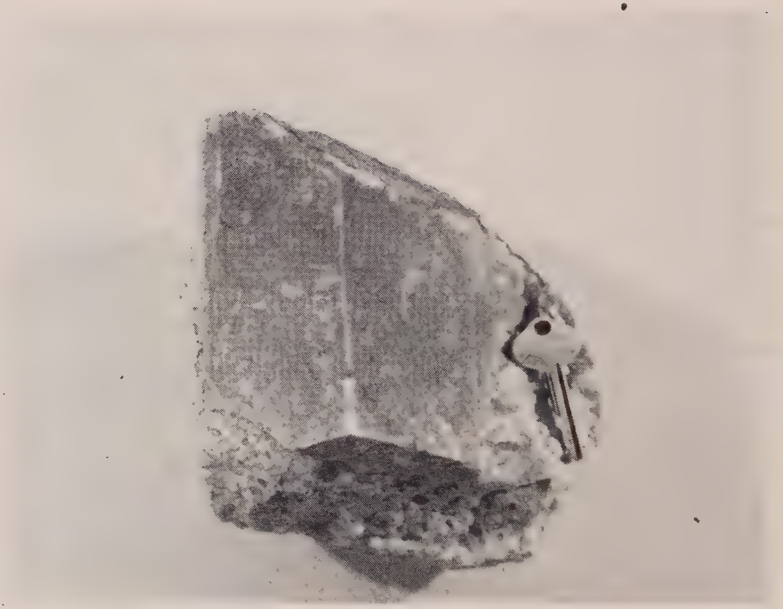

FIG. 14. "Phantom" crystal of perthite with graphically intergrown quartz, Chihuahua Valley, Riverside County, California. This crystal formed the central part of a much larger individual of graphic granite, part of which is still attached. The "phantom" faces are coated with thin scales of muscovite and tiny needles of schorl.

Schaller (35, pp. 274-275), Landes (27, pp. 371-398, 401-409; 28, pp. 549-558), Hess (18, pp. 293-296), Gevers (15, pp. 351-375), and many others. In contrast, there appears to be no comparable textural or structural evidence to indicate that the giant crystals themselves are pseudomorphous after other minerals, or that they developed by replacement of earlier solid material in any other way.

The case for replacement

Relations of individual crystals

In analyzing the numerous and well known arguments in favor of a replacement origin for giant crystals, one might begin by asking whether size alone is significant in this connection. Some investigators have suggested that there is a limit to the size that a crystal of a given substance can attain by growth under a given set of conditions, regardless of how much material is available for nourishment, and have theorized about the governing factors involved. Such limits might well exist, but they have not been established for growth of crystals from pegmatitic liquids, and it seems doubtful whether they could be set accurately on the basis of information now available. Further, there seems to be no theoretical basis for assuming that single crystals of a given rock-forming mineral can grow to greater size by replacing solid material than by developing directly from a solution; indeed, hundreds of experiments on crystal growth suggest that precisely the opposite may be the case, even though it must be admitted that conditions of growth in most laboratory experiments are not strictly comparable to those that probably obtained during the formation of minerals in intrusive igneous rocks. So far as pegmatite occurrences are concerned, few observers seem to have shrunk from the concept of huge perthite individuals crystallizing from a magma, and it scarcely seems reasonable to reject a similar origin for giant crystals of other minerals on the basis of their size alone.

Remarkably little *direct* evidence for growth of giant crystals by replacement has been recorded in the literature on pegmatities, although, as noted above, replacement relations between relatively fine-grained minerals and earlier, coarser-grained material have been described from hundreds of occurrences. Landes, who gave particular consideration to the origin of large crystals in several pegmatite districts, concluded that the huge spodumene "logs" in the Keystone, South Dakota, pegmatites were developed by replacement of earlier formed magmatic minerals. He pointed out (28, p. 548), in support of this conclusion, that these crystals "exhibit cross cutting relationship to the other minerals in the pegmatites," but frankly acknowledged that "in the Etta mine they are so huge that this characteristic is not easily observed, but in the Hugo mine a small spodumene crystal passes directly through a large apatite individual."

Evidently the cross-cutting relations of these giant crystals are not wholly convincing as evidence for replacement. Although the writer has had no opprotunity to examine these Black Hills occurrences in detail, he has made careful studies of fourteen large exposures of similar giant-textured quartz-spodumene pegmatite in the Southwestern States. In none of these occurrences was it possible to demonstrate a cross-cutting of quartz by spodumene in a manner suggesting replacement; instead, the quartz was found to occur as separate, diversely oriented crystals impinging on opposite sides of a given prism of spodumene (Fig. 15). Similar relations appear to be characteristic of the quartz and feldspars that are associated with giant prisms of tourmaline and beryl at other localities. And if these relations are as characteristic as they seem to be, one can only agree with Shaub (37, p. 681) that there is little structural evidence in pegmatites that indicates or even strongly implies transection of earlier solid material by giant crystals of elongate habit.

Even a demonstrable "penetration" or "separation" of one large indi-

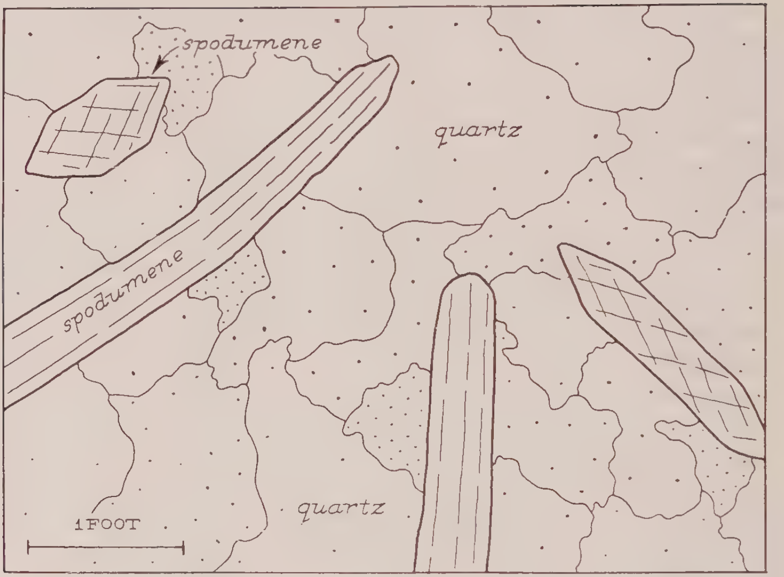

FIG. 15. Giant pegmatitic texture in quartz–spodumene pegmatite, Midnight Owl mine, White Picacho district, Arizona. Note how spodumene crystals are enclosed by an aggregate of diversely oriented, anhedral crystals of quartz. Contacts between quartz crystals are diagrammatic in detail, but nearly all are correct in position to within an inch.

vidual by another, as in the single occurrence specifically cited by Landes (28, p. 548), can be interpreted in more than one way. The same relations could be the result of nearly simultaneous crystallization from a liquid, with one crystal partly enveloping the other. The frequency of such occurrences would be a function of several factors such as the number, positions, and orientations of the crystal nuclei and the disposition of growth-rate vectors for the respective crystal lattices. Moreover, detailed examination of the mineral contacts in such occurrences from several pegmatite districts repeatedly reveals the presence of tiny apophyses, veinlets, and other features that suggest initial development of the "penetrating" crystal, followed by growth of the other crystal around it (Fig. 16).

Landes (28, p. 548) also noted irregular and abrupt changes in the thickness of the spodumene crystals in the Etta mine, and attributed these changes to differences in replaceability of the earlier minerals at whose expense the spodumene was formed. Although one might expect more even growth in a crystal forming from a liquid, as he suggested, a distinct uneveness does seem to be characteristic of many crystals that are developed very rapidly, particularly when they reach large sizes. As pointed out by Frondel (13, pp. 469-470), several investigators have remarked on the tendency of crystals to become irregular and highly imperfect when grown to large sizes in the laboratory. Perhaps more important with respect to the spodumene logs in the Etta mine is the possibility that they were competing for space with very large crystals of quartz and other minerals during a period of essentially contemporaneous growth, so that the irregularities of form might reflect to some degree the available space in a crystallizing mesh of extremely coarse texture. Minerals of much smaller grain size evidently developed later, and obscured some details of the earlier crystal boundaries.

Inclusions of other minerals are scattered through many giant crystals in pegmatite, and have been interpreted by some observers as residua of earlier crystals that were in large part replaced during growth of the giant hosts. These inclusions, which commonly are diversely oriented and show rounded, smooth surfaces, might be alternatively viewed as small, growing crystals that were caught and enclosed by the much more rapidly growing lattices of the giant hosts. One might expect such crystals to be subhedral or euhedral, however, as pointed out by Landes (28, p. 548).

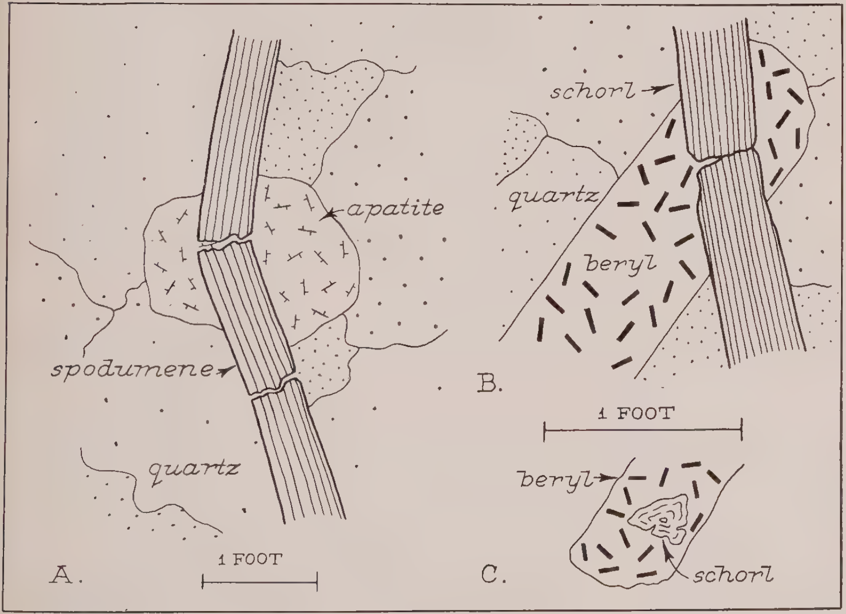

FIG. 16. Typical examples of older crystals "penetrating" younger crystals. *A*. Fractured prismatic crystal of spodumene, in part surrounded by younger crystal of apatite, Midnight Owl mine, White Picacho district, Arizona. *B*, *C*. Long prisms of schorl in part surrounded by younger crystals of beryl, Fano mine, Riverside County, California.

To the writer, they seem most readily explained in terms of very rapid crystallization of the host individuals from a silicate liquid, with entrapping of droplets and globules of the liquid (or of crystals and liquid) by these giant individuals; subsequent crystallization of the trapped liquid would yield inclusions that would nearly fill the rather smooth-walled spaces occupied by the globules of liquid. Upon crystallization, the included liquid should contribute some material to the host crystal and some to the final inclusion, in proportions depending upon the composition of the liquid. The actual occurrences are in accord with this, as nearly all the inclusions are mineralogically identical with the other large crystals that flank or partly enclose the giant hosts. Thus the spodumene crystals in giant-textured quartz-spodumene pegmatite commonly contain small, rounded inclusions of quartz (with very minor amounts of albite and other minerals).

The problem of support

How could a giant crystal be supported during its growth from a liquid? This question has been raised most frequently with reference to crystals of spodumene (see, for example, 18, pp. 290–295; 9, pp. 238–239; 28, pp. 547–549), whose specific gravity is distinctly greater than that usually adduced for a pegmatite magma. Several investigators who favor a replacement origin for such crystals have suggested that, had they been formed in a thin, watery pegmatite solution, they would have sunk rapidly in this liquid, even if originally attached to solid material. This view seems a little extreme, and may represent some confusion between the effects of specific gravity and those of viscosity of the solution.

Let it be assumed, however, that a combination of mechanical disturbance in the system and a difference of say 0.5 to 0.8 in specific gravity between spodumene crystals and the postulated enclosing liquid invariably were sufficient to cause detachment of the crystals and subsequent sinking in the liquid. It then would be necessary to call upon replacement inward from a single horizon in the pegmatite body to account for such fringing or comb-like arrangements as those so well exposed, for example, in the Harding mine (Fig. 1). This presents structural difficulties of the type summarized and discussed by Cameron, et al. (8, pp. 101–105) in connection with the genesis of pegmatite zones. Other advocates of a replacement origin have recognized the existence of "comb and concentric structures in the solidified pegmatites" (18, p. 291), and even have agreed to the significance of these structures in terms of primary crystallization, but in effect they have dismissed the matter by suggesting that such features are quantitatively unimportant.

The problem of support during crystallization from a liquid has been regarded as most critical in connection with those giant prisms that show no preferred orientation, and also with those that form huge, radial groups. It has been concluded, reasonably enough, that these crystals could not have grown in a liquid without some means of support. The assumed absence of such support, however, appears to rest wholly on an earlier assumption that large crystals, or crystal groups, of a single mineral were formed separately during a given period of time, without concomitant crystallization of any other mineral species. But is this earlier assumption trustworthy? The writer can see no reason why crystallization of two or more minerals should not have taken place penecontemporaneously to form a loose mesh whose interstices were progressively filled in by the growing crystals. Quartz is the most common mineral that is interstitial to giant crystals of spodumene and other minerals, and in such occurrences it forms giant crystals of its own. It appears to have developed with and slightly after the other minerals, so far as its known textural relations are concerned.

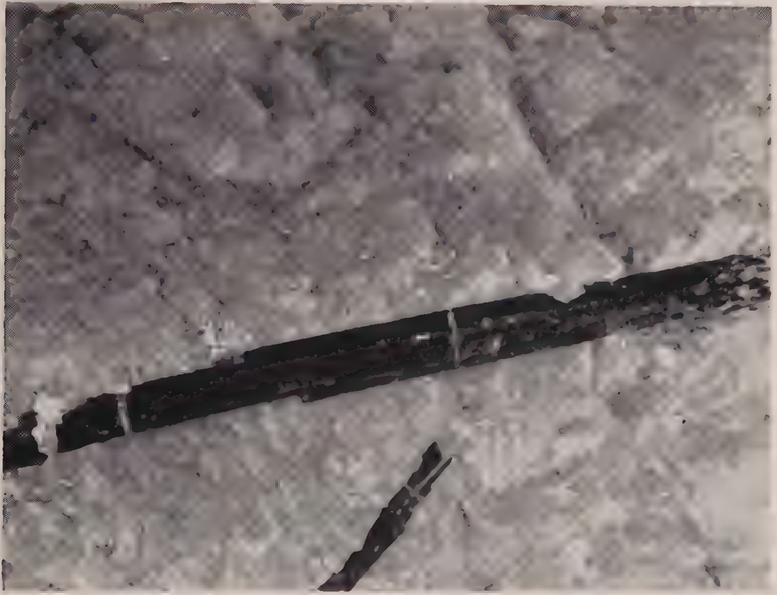

FIG. 17 "Healed fracture" structure in black tourmaline. Southern Pacific silica quarry, Riverside County, California. The fractures are filled with quartz, which occurs in part as apophyses from the large crystals of quartz that flank the prisms of schorl. The large prism is about 3 inches thick.

That support of the kind here suggested must have existed during development of many giant crystals is demonstrated by "healed-fracture" structures in numerous occurrences of spodumene, tourmaline, and other minerals of slender, elongate form. Typical examples, well exposed in the face of the Southern Pacific silica quarry near Nuevo, California, are shown in Figs. 17 and 18. Very large prisms of schorl here are broken along many irregular, transverse fractures that are filled with quartz, and some of the segments show evidence of rotation or other movement prior to the filling. The fractures have matching walls, and evidently were formed as simple tensional breaks, perhaps as a result of minor disturbances in a very coarse but fragile crystal mesh of tourmaline and quartz. These fractures then were filled with quartz, much of which is crystallographically continuous with the giant quartz individuals that flank the schorl prisms. The filling thus appears to have been accomplished during the final stages of consolidation in the rock. These relations are not readily explainable in terms of a replacement origin for the schorl, especially as the fractures do not extend beyond the margins of the schorl crystals. It is not easy to imagine how the tourmaline prisms could have been fractured, pulled slightly apart, and in some instances disturbed on a larger scale after their development by replacement of solid pegmatite, without appropriate fractures appearing somewhere in the adjacent minerals.

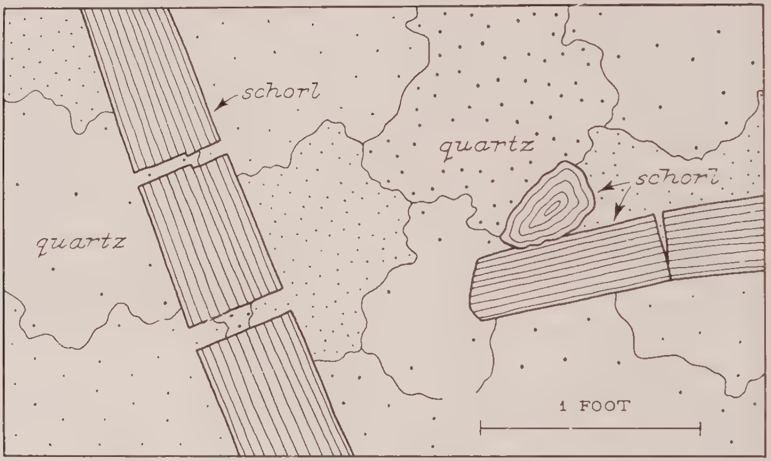

FIG. 18. "Healed-fracture" structure in very coarse-grained quartz—schorl pegmatite, Southern Pacific silica quarry, Riverside County, California. Fracture-filling relations indicate that the schorl prisms are older than at least some of the flanking anhedral crystals of quartz.

The stellate, or rosette-like, arrangement of many giant crystals has been thought by some observers to pose a serious problem of support during any postulated growth from a liquid; indeed, Hess (18, p. 295) has stated that "radial disposition in three dimensions, with crystal terminations of the minerals at the outer ends, may, I believe, be accepted as a sign of replacement." This suggestion appears to have stemmed mainly from a study of huge spodumene rosettes in the Etta pegmatite of South Dakota, where many crystals several feet long radiate outward from small masses of fine-grained pegmatite into pegmatite that consists mainly of very large, anhedral crystals of quartz. In describing these fine-grained masses, Hess (19, p. 456) stated that " . . . they contain apatite,

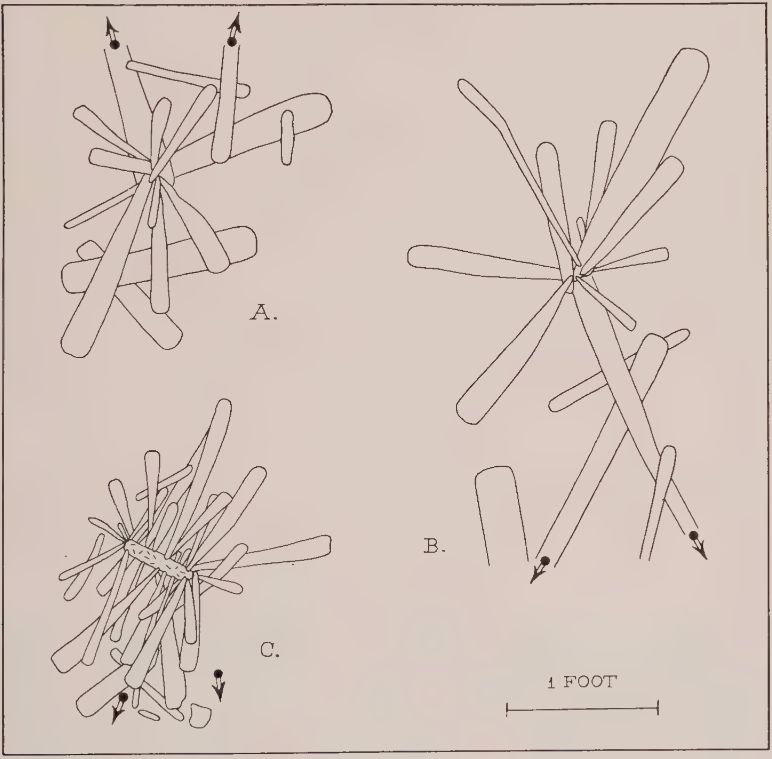

Fig. 19. Radial distribution of spodumene prisms in very coarse-grained quartz—spodumene—amblygonite pegmatite, Midnight Owl mine, White Picacho district, Arizona. Those prisms essentially coplanar with the exposed surfaces of the pegmatite are the only ones shown. Arrows indicate probable directions of attachment and support of crystals during growth; all sketches show relations on vertical faces of quarry. *A*. Growth from ends of two crystals attached to finer-grained pegmatite above. *B*. Growth from ends of crystal attached to finer-grained pegmatite below. *C*. Growth that may have begun as a crystal fringe from finer-grained pegmatite in hanging-wall part of pegmatite body, followed by detachment of a tabular mass of this pegmatite (with its fringe), sinking to a lower level, and completion of fringe on opposite side of the mass.

triplite, muscovite in plates an inch across, some quartz, potash feldspar, and other minerals, and are replaced masses of country rock."

If the spodumene crystals grew radially from masses of partly digested country rock, one might extend the problem back in time, and ask how these masses were supported within the pegmatite body. They might well represent detached fragments of wall rock that were scattered through a fragile, rapidly growing mesh of spodumene and quartz crystals. Detachment might have taken place after consolidation of the relatively thin outer zones of the pegmatite, or perhaps at an even earlier stage. Crystals of elongate habit could be expected to grow radially outward from the small masses of wall rock, the temperatures of which probably were slighly lower than that of the pegmatite fluid. Support would be provided by the crystal-bearing liquid or by the crystal mesh itself, perhaps very uncertainly at first but more and more stoutly as the crystals of both spodumene and quartz grew.

Similar, somewhat smaller-scale occurrences were studied by the writer in several pegmatite bodies in western Arizona, where outcrops and quarry exposures show evidence that some spodumene rosettes were supported during growth by other crystals of quartz and spodumene (Fig. 19). Such evidence is lacking in the exposures of other rosettes, to be sure, but this might be attributed to lack of complete exposure in three dimensions.

Other arguments

An argument commonly advanced to support the replacement theory is that random or erratic distribution of giant crystals and highly unsystematic variations in pegmatite textures are not easily explained in terms of fractional crystallization from a melt. This proposition might be true enough if such relations really were characteristic of pegmatites, but the mineralogical and textural variations in these rocks—especially where they involve crystals of giant size—are remarkably systematic. This has been pointed out in previous paragraphs, and has been noted and carefully documented by dozens of investigators during the past 80 years (8, pp. 11-13). The very absence of wholly erratic and unsystematic features from the zonal pattern of pegmatite bodies consitutes one of the strongest arguments for the development of the zones by primary crystallization from a magma.

The concentration of rare minerals, some of which form very large crystals, has been cited as evidence of the activity of hydrothermal solutions in many masses of pegmatite. Hess (18, p. 292), for example, has stated that "So far as I know, no suggestion adequately accounts for the excessive quantitites of minerals of low solubility such as the columbites, that, under these (magmatic) theories, must have been held in solution, and none satisfactorily explains the presence together of minerals considered as characteristic respectively of high and low temperatures." The term "solubility" is a little puzzling, as used in this statement, because the columbites, though almost insoluble in water, might well be very soluble in a pegmatitic rest-liquid developed during fractional crystallization of a granitic magma. The known segregation in a cooling magma of relatively rare elements such as beryllium, columbium, and lithium is accomplished mainly because these elements are not readily admitted into the crystal lattices of most common rock-forming minerals that are stable at high temperatures; ordinarily such elements cannot form lattices of their own until they are sufficiently concentrated in the rest-magma by fractional crystallization of other minerals. This bespeaks considerable solubility, whether these rare elements are fixed in crystals developed directly from the liquid or leave the liquid as constituents of hydrothermal solutions at some late stage during differentiation.

The occurrence together of minerals ordinarily regarded as forming in markedly different temperature ranges, such as perthite and cookeite or spodumene and zeolites, is readily explainable in terms of replacement, as Hess and others have suggested. Further, the textural relations of such minerals commonly indicate that one was formed largely at the expense of the other. In contrast to this, no giant crystals, or other minerals indigenous to pegmatite zones, are known to show such anomalous temperature or textural relations with respect to one another, and hence no recourse to hydrothermal replacement is needed to account for the observed associations.

SUMMARY AND CONCLUSIONS

Crystals of giant size, some of them weighing tons or even tens of tons and having maximum dimensions measurable in tens of feet, are constituents of pegmatite in many parts of the world. Perthite and spodumene form the largest known individuals, and among the other species whose crystals reach giant sizes are allanite, amblygonite, apatite, beryl, biotite, columbite, fluorite, hornblende, monazite, muscovite, petalite, phlogopite, plagioclase, quartz, topaz, tourmaline, and triphylite-lithiophilite.

Most of these huge crystals are euhedral, with characteristically simple habit and broad, rough faces. Some are regular in form, whereas others taper from one end to the other, or even from the central part toward both ends. Still others, like the spodumene "logs" in the Etta pegmatite of South Dakota, show irregular and abrupt pinchings and swellings. A few mineral species, notably quartz, form anhedral crystals of great size.

Some of the giant crystals are scattered individually through the mass of pegmatite in which they occur, and others are grouped. Those of elongate habit commonly form gigantic jackstraw-like aggregates, or are clustered in sub-parallel arrangements that appear on exposed surfaces of the containing pegmatite body as huge fringes. Groups of radiating crystals also are known, but are relatively rare.

Nearly all the crystals of exceptional size are found in zoned pegmatites, and appear to be primary constituents of the zones in which they occur. A few very large individuals occur in cavities or pockets that are younger than the surrounding solid pegmatite, but rarely are such crystals as large as other crystals that lie outside the cavities. The giant crystals of the pegmatite zones form phenocrysts in rock with porphyritic texture or are parts of non-porphyritic aggregates that have giant pegmatitic texture. The crystals show systematic trends in their distribution and size, and these trends are in full accord with all systematic structural and textural variations within the pegmatite body as a whole. Like the lithologic zones that contain them, they appear to have developed successively from the outer parts of a given pegmatite body inward toward its center.

Many investigators have concluded, on the basis of detailed study, that pegmatite zones were formed by fractional crystallization of a magma, with incomplete reaction between successive crops of crystals and rest-liquid (8, pp. 79-106). The giant crystals in pegmatites are here considered to be primary constituents of these zones, mainly on the basis of their distribution, textural and structural relations, and variations in composition.

The most convincing evidences of replacement within pegmatite bodies —mainly pseudomorphism, transection and corrosion of one mineral by another, and distribution of minerals in rock masses or along channelways that cut across earlier minerals or rock units—are readily applied to relatively fine-grained minerals that plainly are younger than the giant crystals. However, there appears to be little or no evidence for development of the giant crystals themselves by replacement of earlier pegmatite material. The criteria of hydrothermal activity so carefully outlined by Landes (28, pp. 538-539), for example, are not readily applied to the giant crystals, and most features specifically cited in favor of a replacement origin for such crystals seem more readily explainable in terms of primary crystallization from a liquid. Moreover, the usual arguments against a primary origin seem to be refutable in convincing terms by observed features of occurrence.

Available evidence, in the writer's opinion, indicates that nearly all the giant crystals were formed during what has been designated by most investigators the primary, or magmatic, stage of pegmatite development, and hence by crystallization from liquid under conditions that permitted remarkable growth of a relatively few individuals. These conditions will be discussed in some detail in a forthcoming paper. Suffice it to say here that the typical pegmatitic magma that yielded these enormous crystals must have been rich in hyperfusible constituents and probably had a very low viscosity. The crystals are thought to have been formed rapidly under restricted-system conditions involving rather delicate thermal and chemical balance. Temperatures almost certainly were below 600° C., and the confining pressures were sufficiently great to prevent major escape of volatile constituents during the period of giant-crystal development.

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BERYLLIUM MINERALS IN THE VICTORIO MOUNTAINS, LUNA COUNTY, NEW MEXICO*

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Abstract

Beryl, helvite, and beryllian idocrase occur within a small area in the Victorio Mountains, New Mexico. Beryl crystals form the selvage of a quartz-tungsten vein that cuts sharply across flat-lying limestone but which did not alter the limestone visibly. Helvite forms tetrahedral crystals that cut calcite and in turn are cut by grossularite in a nearby coarse-grained silicated marble. Idocrase containing 0.2 per cent BeO is interlayered with fluorite and garnet in tactites at the same locality. Beryllium has been found in other tactites in small amounts, but its form has not been determined.

The Victorio Mountains vein is similar in mineralogy and paragenesis to several known beryl-bearing veins that have been described from other regions.

A modification of the Goldschmidt-Peters theory for the origin of these beryllium minerals is proposed: beryllium occurs as beryl in rocks rich in aluminum with relation to the sum of calcium, sodium, and potassium, and as helvite in aluminum-poor rocks. Following Shand, the aluminum ratio is applied to metamorphic as well as to igneous rocks. In the Victorio Mountains, helvite may have been formed by replacement in marble from solutions originally similar to those that deposited beryl in the open fissures, but with their aluminum content reduced by the formation of garnet in that calcium-rich environment.

Introduction

A unique association of helvite and beryl occurs in the Victorio Mountains, 5 miles south of Gage, Luna County, New Mexico. The area was visited in September 1949, during a survey of nonpegmatite beryllium resources, to investigate a reported occurrence of vein beryl. Most of the day and a half spent in the area was devoted to sampling the prospects and sketching the geology in the vicinity of the known beryllium deposits.

The northern half of the Victorio Mountains, which are 600 feet above the plain, is a gently dipping series of the Tertiary andesite and rhyolite flows that are common in the region. The southern half is composed of flatlying limestones of Paleozoic age that are intruded by small bodies of granitic rock (Darton, 1916, pp. 83–85). Mine Hill, the site of a silver-lead deposit that has been described by Lindgren and others (1910, pp. 290–292), is topped by fossiliferous Fusselman limestone (Silurian). About a mile northwest of Mine Hill, where the beryllium minerals occur (Fig. 1), Gym limestone (Permian) apparently directly overlies Montoya limestone (Ordovician); "while some Fusselman limestone may intervene, no direct evidence of its existence was obtained, and it

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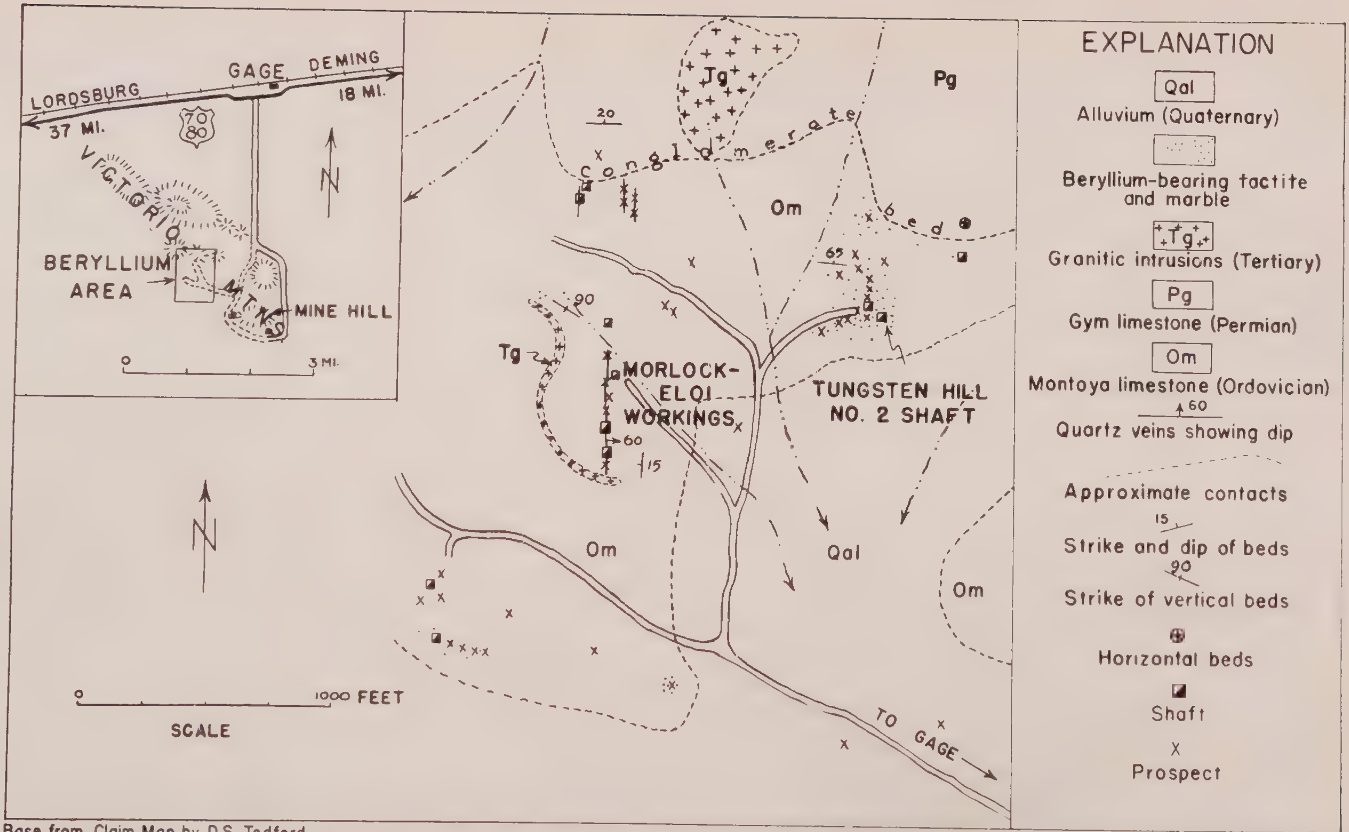
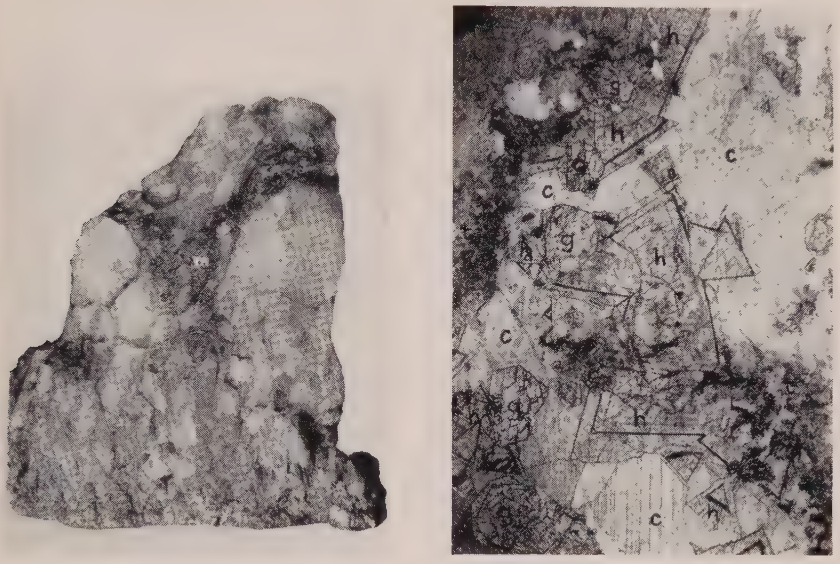
* Publication authorized by the Director, U. S. Geological Survey. Work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.



Base from Claim Map by D.S. Tedford

Stratigraphy after Darton (1916, p 84)

FIG. 1. Sketch map of the Beryllium Area, Victorio Mountains, Luna County, New Mexico.



A

B

FIG. 2. Beryllium minerals. *A*. Hand specimen of quartz vein, ×0.35. Crystals of beryl, *b*, are more or less perpendicular to the contact, which forms the base of the specimen (the contact plane is nearly vertical in outcrop). The beryl crystals are overgrown by crystals of milky quartz, *q*, and the spaces are filled with fine-grained muscovite, *m*. *B*. Photomicrograph of thin section of helvite-bearing marble, ×3.5, ordinary light. Single and twinned tetrahedra of helvite, *h*, nearly enclose rough dodecahedra of grossularite, *g*, in a groundmass of coarsely crystalline calcite, *c*. The dark fibrous material is tremolite, replacing all other minerals.

appears to be cut out either by faulting or unconformable overlap." (Darton, 1916, p. 85). Mine Hill and the beryllium area are apparently separated by a fault, although only minor faults may be seen in the beryllium area.

BERYL DEPOSIT

Lindgren (Lindgren et al., 1910, p. 293) noted a quartz vein containing huebnerite and scheelite on the present Eloi and Morlock unpatented claims, formerly called the Brinkman, Irish Rose, or Kimmick claims. Since his visit, the vein has been irregularly mined for tungsten along part of its 600-foot length. The 1- to 2-foot thick fissure vein has knife-sharp plane contacts against dolomitic Montoya limestone, which has been only slightly altered. The limestone generally retains its fine grain and gray color except locally, where it has been slightly replaced by quartz and grossularite.

Beryl was first recognized at this locality in 1948 by W. P. Johnston of the New Jersey Zinc Exploration Co., Hanover, N. Mexico. Prismatic crystals of beryl are oriented perpendicular to the wall (Fig. 2*A*) in a hanging-wall selvage. The beryl crystals, as much as 5 cm. long and 1 cm. in diameter, are invariably bounded by $(10\bar{1}0)$ and (0001) forms. The beryl is very pale green (5G9/2; Munsell Book of Color, Baltimore) to colorless. It has an ordinary refractive index of 1.5740±0.001, corresponding to a composition of about 13.5 per cent BeO.[1]

Quartz and some fine-grained muscovite make up most of the vein. The tungsten mineral for which the deposits were mined is wolframite; it was not present in sufficient amounts in the material available to determine its relations with the other minerals. Fluorite is rare, and galena, pyrite, wulfenite, lead carbonates, and scheelite have been reported (Hess, 1908). A beryl-bearing selvage is not evident along much of the length of the vein; nevertheless the whole vein averages 0.06 per cent BeO, 0.09 per cent tungsten, and 0.00X per cent molybdenum. The variations of beryllium and tungsten are not correlative in the analyzed material from various parts of the vein.

HELVITE DEPOSIT

Helvite occurs a few hundred feet east of the quartz vein on the Morlock and Eloi claims, in irregular lenses and bands of marble and tactite surrounded by unaltered Montoya limestone. The bands apparently are parallel to the bedding. The tactite is not near any exposed intrusion, although a small mass of granite porphyry crops out on the hill north of the altered rock (Fig. 1). The alteration, which is generally most intense in the more steeply dipping parts of the beds, may be related to a fault a mile to the east mapped by Darton (1916, p. 84). One of the veins at the top of the outcrop of the Montoya, north of the Morlock-Eloi workings (Fig. 1) is bordered by a small amount of tactite (L. R. Page, personal communication).

The helvite was discovered in dump material from the Tungsten Hill No. 2 shaft by W. I. Finch of the U. S. Geological Survey. The shaft was inaccessible, and helvite could not be found in rocks at the surface near the shaft. The helvite is in a coarse-grained massive silicate marble, composed of about 30 per cent calcite, 20 per cent grossularite, a maximum of 10 per cent helvite, a small amount of augite, and about 40 per cent tremolite that has irregularly replaced calcite and other minerals. The color of the helvite is moderate yellow (3Y7/8). The mineral occurs scattered through the calcite as sharp tetrahedra, 5 mm. across, with no modifying faces. Some crystals are twinned on (111). The helvite has a refractive index of 1.735 ± 0.005 and a specific gravity of 3.25, corresponding to a composition of about 85 per cent helvite and 15 per cent danalite (Glass et al., 1944, p. 183). In thin section (Fig. 2*B*), the helvite is pale yellow, isotropic, and shows some dark peripheral zones of very fine grained inclusions, similar to the helvite from Casa La Plata, Cordoba Province, Argentina, and Schwartzenberg, Germany (Fischer, 1925, p. 146). Helvite is most easily recognized in the Victorio Mountains by its tetrahedral form. The color is distinctive, yet similar to that of the grossularite, vanadinite-mimetite, and serpentine in this district.

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[1] Unpublished chart by W. T. Schaller, U. S. Geological Survey.

Yellow or brown grossularite, in small rough dodecahedra, is a common associate of helvite. It has the peripheral anisotropic zoning and dodecahedral twinning characteristic of garnet from some limestone replacements (Holser, 1950, pp. 1082–1083). Some peripheral zones have been replaced by calcite, which is euhedral to subhedral where it is in contact with helvite (Fig. 2*B*).

Closely associated with the helvite-bearing marble is a tactite in which bands of idocrase and fluorite alternate with bands of garnet and tremolite that have been largely altered to talc. The idocrase occurs as radiating clusters about 3 mm. in diameter. It is anomalously biaxial negative, with a very small 2V and very low birefringence. The index of refraction N_x or N_y is 1.701 ± 0.002. Spectrographic analysis of hand-picked grains showed 0.2 per cent BeO.

Spectrographic analyses of 12 samples of tactite and marble from various parts of the area showed 0.002 to 0.1 per cent BeO. These samples include metamorphosed limestone from the pediment south of the quartz vein, from one locality west of the vein, and from the slightly metamorphosed wall rock of the vein (Fig. 1). Near the north end of the vein, where it contained 0.2 per cent BeO over a width of 2 feet, a 2-foot layer of rock in the hanging wall contained 0.02 per cent BeO. Several samples were fractionated in heavy liquid. The heavy separate (mostly grossularite and psilomelane type manganese oxides) was tested for helvite by staining (Gruner, 1944), and the light separate (mostly carbonates) was examined optically for beryl. In several thousand grains examined, no grain of either helvite or beryl was found. Grossularite was separated from the richest (0.1 per cent BeO) helvite-free tactite but was found to contain only 0.007 per cent BeO. The mode of occurrence of beryllium in these tactites is, therefore, not yet known, but in the tactite at Iron Mountain, N. Mex., comparable amounts are distributed in several silicates and an unidentified alteration product (Jahns, 1944*b*, p. 58).

The tactites contain scheelite; analyses show a range in tungsten content from less than 0.01 to 0.06 per cent. Lead, zinc, and silver are also present in local concentrations.

TABLE 1. MINERAL ASSOCIATIONS OF VEIN BERYL

Area	Locality	Mineral associations*											Remarks	References
		Beryl	Wolframite	Scheelite	Cassiterite	Molybdenite	Other sulfides	Quartz	Muscovite	Fluorite	Tourmaline	Other gangue		
Victorio Mts., N. M.	Eloi claim	R^{1}	R^{2}	V				A^{2}	C^{3}	R				First report
Little Dragoon Mts., N. M.	Bluebird mine	V	R	R				A		C				Galbraith, 1947, p. 83
	Tungsten King mine	R$^{1?}$		R^{3}				A^{2}	C^{4}			R^{1}		First report†
Hualpai Mts., Ariz.	Boriana mine	R	C^{2}	C^{3}		R	C^{3,4}	A^{1,5}		C				Hobbs, 1944, pp. 254–255
Lone Pine, Calif.	1½ miles southeast	C												Murdoch and Webb, 1948, p. 70
Chaffee Co., Colo.	California mine	C^{1}				C^{3}		A^{1}	C^{2}	R^{4}				Landes, 1934; Adams (in prep.)
Hill City, S. D.	Cowboy mine, Mohawk mine, and others	C^{1}			R^{1}			A^{2}	C^{1}					Page, et al (in prep.)
Marietta, Nev.	Pine Crow claim	R^{2}	R^{2}					A^{1}						First report‡
Irish Creek, Va.	Irish Creek mine	C^{2}	V^{2}		R^{2}		V^{3}	A^{1}	A^{2,3}	A^{3}		C^{3,4}	Phenakite^{3}	Koschman, et. al., 1942, pp. 279–282
Muzo, Colombia	Muzo mine and others	C^{2}					R	R		R		A^{1}		Oppenehim, 1948, pp. 35–36
San Luis Province, Argentina	Loma Blanca mine	C		C				C	A	R				Kittl, 1930
	Cerro Morro mine	V		C			V	A	A	C				Smith and Gonzales, 1947, p. 8
Catamarca Province, Argentina	San Antonio mine	V	C					A						Smith and Gonzales, 1947, p. 31
Cornwall, England§	South Crofty mine, Illogan	R^{1,2}			C^{1}			A^{1}	C	C^{1}	A^{1}	A^{1,3}	Bertrandite^{3}	Hallimond, 1939
	Beam mine, St. Austell	R			C						A			Phemister, 1940
Buryat-Mongolia, USSR.	Dzhidin mine	R^{6}	C^{4}			R^{3}	C^{5}	A^{2}	C^{2}	C^{4}		C^{1,6}		Smolyaninov, 1940
Boevska, Cheliabinskia, USSR.	?	R	C	C			R	A	C		R			Sushchinsky, 1916
Kazakhatan, USSR.	Akchatau mine	R^{2}	C^{4}	R^{7}	V^{3}	R^{9}	R^{5}	A^{1,4}	C^{4}	C^{4}	V^{8}	C^{6}		Pinus, 1940
Onon, Chitinskia, USSR.	Schorl Mtn.	A^{2}	C^{3}		R^{2}	R^{3}	R^{7}	C^{1}	R^{5}	C^{6}	R^{7}	C^{4}	Same paragenesis ?	Tetyaev, 1918
	Alman'	C	C			R	R	C	R	C		C		Fersman, 1940, pp. 120–121, 569–570
	Golshoy Soktuy	R				R	A	A	R	C		R		
	Pervonachalny mine	V			C		A	A		C		R		
Ch'ungch'ong-pukto, Korea	Taemy'ong mine	C	R					A						Gallagher, et al, 1946
	Naeson-Puyong mine	R	C	R		R	R	A		R				
	Chungch'on Ch'ongyang mine	C	C			R	R	A						
Central Honshu, Japan	Ebisu-Takane mines	R	A^{3}		R^{2}	C^{3}	A^{4}	A	R	C^{1}	R^{1}	C^{1}		Takimotu, 1944
Yuntaishan district, Kiangsi, China	Wati mine	R	A^{1}	C^{1}	C^{2}		C^{4}	A	R		R^{1}			
	Sihuashan mine	R^{7}	C^{5}	R^{8}	R^{6}	C^{4}	R^{9,12}	A^{10,11}	C^{2}	C^{11}		C^{3,7,13}	Same paragensis	Hsu and Ting, 1943*b*, p. 67; 1943*a*, p. 272
	Shunglungkou mine	R	C	R	C	R	R	A	C	C		C		———, 1943*a*, p. 192
	Tangping mine	V	C		R	R	C	A	C	C		R		———, 1943*a*, p. 198
Southern Shan States, Burma	Mt. Byingi	C	C			C								Brown and Heron, 1909, p. 102

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* Approximate proportions of minerals as inferred from published descriptions: A—abundant; C—common; R—rare, V—very rare. Superscripts indicate paragenesis where known.

COMPARISON WITH OTHER LOCALITIES

Beryl in quartz veins similar to the vein in the Victorio Mountains has been widely reported, as summarized in Table 1. In most of these localities the beryl is rare; it is usually associated with tungsten minerals, fluorite, and, to a lesser extent, cassiterite or molybdenite. Beryl occurs also in the unique carbonate veins of Muzo, Colombia. The paragenesis of beryl in many of these localities has not been recorded.

Thousands of beryl-bearing pegmatites have been described, many of them rich in quartz and tabular in shape. In compiling Table 1, a distinction between pegmatite and quartz veins was made on the basis of the presence or absence of feldspar. This follows a classic definition by Haidinger (1845, p. 585); its significance with relation to quartz-rich dikes or veins was pointed out by Tolman (1931, p. 296). Admittedly the distinction is somewhat arbitrary, as many examples of gradation between the two have been described. (See compilations by Tolman, 1931, and Furnival, 1939.) Fersman's work emphasized the genetic relation of many quartz veins to pegmatites (1940, pp. 37–39). The fracture fillings that form distinct units of many pegmatites are commonly composed of quartz, but many contain other pegmatite minerals, including beryl. Some of the quartz-rich fracture fillings are continuous and contemporaneous with the quartz core or other inner zone of the associated pegmatite (Cameron et al., 1949, pp. 70–83, 105-106). Some beryl-bearing veins in Quebec (Norman, 1945, pp. 15 16) and in New South Wales (David, 1887, pp. 112–113; Carne, 1911, pp. 58, 67) contain small amounts of feldspar and seem to be transitional between quartz veins and pegmatites. The quartz veins of Chaffee County, Colo., Hill City, S. Dak., Irish Creek, Va., San Luis Province, Argentina, Onon, U.S.S.R., and southern Kiangsi, China (Table 1) are all said to be closely related to neighboring pegmatites.

These many examples suggest that beryl-bearing quartz veins have origins similar to those of beryl-bearing pegmatites. They were probably formed at temperatures higher than those of most other mineral veins. Bodies so rich in quartz probably were deposited from aqueous solutions. (See, for example, Furnival, 1939.) (According to Jahns, 1948, they are magma-like solutions.) A late-pegmatitic to early hydrothermal stage is also favorable for the deposition of the frequently associated tungsten minerals (Kerr, 1946, pp. 38–39). Although no pegmatite was found in the Victorio Mountains area, the quartz-beryl vein is probably a high-temperature hydrothermal type.

Helvite in veins is associated with rhodonite, rhodochrosite, and quartz (Silverton, Colo.: Burbank, 1933; Butte, Mont.: Hewett, 1937; Kapnik, Hungary: Szabo, 1882), and in each vein helvite was late in the sequence of mineral deposition. The mineralogic and paragenetic contrast of the two types of beryllium-bearing veins is evident.

The occurrence of helvite in the Victorio Mountains is superficially similar to some other occurrences of the mineral that may also be pyrometasomatic. In most of these, however, helvite formed very late in the mineral sequence, commonly having been deposited in open spaces with fluorite and quartz (Baerum, Kjenner, Rien, and Aamot, Norway: Goldschmidt, 1911, pp. 65, 88, 101, 394–399; Schwarzenberg, Germany: Beck, 1904, p. 60; Carpenter district, N. Mex.: Weissenborn, 1948; Iron Mountain, N. Mex.: Jahns, 1944*a*, p. 195; Lupikko, Finland: Trustedt, 1907, pp. 270–271, Eskola, 1951, p. 71; Bartlett, N. H.: Huntington, 1880). Its origin is probably closely related to that of hydrothermal vein helvite. At Iron Mountain, N. Mex., much of the helvite was deposited at the same time as magnetite tactite, just prior to filling of open spaces. The paragenesis is probably similar at Lupikko, Finland, and Bartlett, N. H., where large amounts of magnetite are likewise present.

At Hortekollen, Norway, helvite occurs both in magnetite-fluorite tactite and along fissures in silicate tactite (Goldschmidt, 1911, pp. 93, 395). The euhedral form of the helvite caused Goldschmidt to infer that it was deposited at an early stage in the metamorphism; but its place in fissures and the association with magnetite-fluorite tactite make a later deposition more probable. At both Iron Mountain and Hortekollen the helvite certainly formed later than the silicate tactite. Beryllian idocrase is among the silicates at both these localities (Jahns, 1944*b*; Goldschmidt and Peters, 1932), as at Victorio Mountains.

In contrast with the other occurrences in metamorphic rocks, the helvite of Victorio Mountains is associated neither with magnetite nor with andradite and hedenbergite. Furthermore, the silicates are euhedral against calcite, in a texture typical of contemporaneous metamorphic recrystallization (Harker, 1939, p. 38). The only mineral having a penetrative replacement texture is tremolite (Fig. 2). The Victorio Mountains helvite deposit thus shows no signs of the iron metasomatism of later lower-temperature and typical replacement form, which preceded or accompanied beryllium deposition in other localities.

The Victorio Mountains helvite occurrence resembles in some respects the helvite occurrence at Casa La Plata, Cordoba Province, Argentina (Fischer, 1925). There helvite occurs in tactite and marble associated with feldspar, fluorite, calcite, quartz, mica, garnet, and idocrase. The deposit is adjacent to an intrusion of pegmatite, however, and it is difficult to assess the relative contributions of intrusion and metamorphism (Fischer, personal communication, 1951).

RELATIONS OF HELVITE AND BERYL

Beryllium concentrations in veins and metamorphic rocks are so unusual as to suggest that the two deposits, so closely situated in the Victorio Mountains, are related in origin. Their age relations were not proved in this preliminary investigation, although the one occurrence of tactite next to the vein suggests contemporaneity. The quartz vein is cut off at its southern end by a small dike of rhyolite porphyry, but the intrusion of this and similar rocks does not seem to be directly related to the areas of tactite and marble.

In any case, the proximity of beryl and helvite in this area suggests reconsideration of the general question of their relative modes of occurrence.

Goldschmidt and Peters (1932) postulated that the beryllium in magmas with mole ratio $(Na_2O+K_2O)/Al_2O_3$ less than 1 ("plumasitic magmas") will crystallize as beryl, chrysoberyl, or euclase; and in those with a ratio greater than 1 ("agpaitic magmas") it will crystallize as leucophanite or meliphanite. Helvite could form from either type of magma. Stability of complex aluminum-oxygen ions in the magma was adduced to explain this difference in mineralogy.

The influence on rock mineralogy of the proportion of aluminum in magma has long been recognized, but it is perhaps most explicitly stated in Shand's classification of igneous rocks (1947*a*, pp. 227–228). The chemical relations of the solid crystals are sufficient to explain the mineralogical differences found, without recourse to any particular ionic situation in the magma. Furthermore, as Shand points out elsewhere (1947*b*, pp. 196–197), the concept is equally applicable to equilibrium relations within metamorphic facies.

If the aluminum ratio for beryllium minerals is to be extended to metamorphic rocks, the virtual absence of beryl in metamorphosed limestone,[2] in contrast with the many occurrences of beryl in aluminous schists around pegmatites,[3] suggests that calcium should be added to the alkalies in the ratio. As for helvite, much of it occurs in the highly calcic environment of metamorphosed limestones. These facts suggest that in an environment of low alumina ratio helvite tends to be deposited exclusive of beryl.

Beryl occurs in many veins with muscovite (Table 1), which requires a high alumina ratio for its formation. The helvite veins do not contain calcium-, sodium-, potassium-, or aluminum-bearing minerals, so the

[2] One occurrence of beryl in marble has been noted by Chhibber (1945).

[3] The best example is the emerald region of the southern Urals (Fersman, 1929).

pertinent chemistry of the solutions that formed them is unknown, aside from an evident excess of manganese.

The principal beryllium mineral of pegmatitic rocks is beryl, although chrysoberyl or phenakite occur in some beryl-bearing pegmatites. All beryl-bearing pegmatites also contain muscovite and other minerals rich in alumina, which indicates that the alumina/alkali ratio of the entire pegmatite is high and that it would be characterized as peraluminous in Shand's nomenclature. In some of these pegmatites the beryl has crystallized early in the formation of the narrow border zone, preceding or accompanying the first feldspar, which is usually perthite or albite (Cameron et al., 1949, pp. 26–27).

The scattered occurrences of beryllium minerals other than beryl in pegmatites are difficult to evaluate and reconcile with the Goldschmidt-Peters theory. It is true that leucophanite or meliphanite are found in the peralkaline nephelite syenite pegmatites of southern Norway, and this was apparently the basis of Goldschmidt and Peter's theory. However, helvite also was deposited in these dikes, and as a relatively early magmatic mineral rather than the late druse filling that is characteristic of leucophanite and meliphanite. Another beryllium mineral in this area, eudidymite, is an alteration product of leucophanite or meliphanite (Brögger, 1890, pp. 148-165, 277, 285). Inasmuch as these three minerals have not been found at any other locality, they are of little use in the general geochemistry of beryllium. Genthelvite occurs in the peralkaline granite pegmatite of St. Peters Dome district, Colorado. (Genthelvite: Adams, personal communication, 1951; pegmatite: Landes, 1935), and danalite in the subaluminous granite pegmatite of Rockport and Gloucester, Mass. (Warren and McKinstry, 1924). On the other hand, helvite occurs in several peraluminous granite pegmatites, even in the same pegmatite with beryl,[4] and with corundum in what is probably a syenite pegmatite (Kityaev, 1928).

Summarizing the suggested changes to the Goldschmidt-Peters theory it is postulated that the stable beryllium mineral in alumina-rich rocks [$(Na_2O+K_2O+CaO)/Al_2O_3$ less than about 1, equivalent to peraluminous rocks in Shand's nomenclature] is beryl, and in aluminum-poor rocks it is helvite. This postulate is now without reference to a magma, or to complex ions or any other condition within the magma. Otherwise stated, where more alumina is present than necessary to form feldspars or similar minerals, beryl may crystallize; where less alumina is present, beryl may not form and the beryllium may remain to crystallize as helvite. Although somewhat obscured by the discussion of magmatic ions, this idea was implicit in Goldschmidt and Peters' recognition of the association of beryl with muscovite. The occurrence of these minerals may thus be controlled by chemical conditions rather than by physical conditions such as temperature and pressure. The mechanism by which the chemical conditions control the mineralogy is not stated, although the extension of the theory to metamorphic rocks where an equilibrium situation exists casts doubt on the necessity of postulating complex ions to control the alumina content of the crystallizing magma.

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[4] At Amelia, Va., helvite was found with spessartite as the last mineral to crystallize, beryl having formed earlier (Fontaine, 1883). At Miask, Ilmen Mountains, U.S.S.R., the very rare helvite apparently was in a granitic pegmatite, and other pegmatites in that area contain beryl (Fersman, 1940, p. 164).

In the Victorio Mountains, the beryl and helvite could have been formed from solutions originally of identical aluminum-rich composition, at the same temperature and pressure. In the open fissure the wall rock would have little effect, and beryl would have crystallized. In the tactite, permeation of the solution into limestone would have changed the composition of the system, the excess aluminum being removed to form grossularite and idocrase, causing the crystallization of helvite. Detailed study of the Victorio Mountains occurrence, not possible in the brief time available, may provide a firmer basis for general application of the theory.

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LIPSCOMBITE: A NEW SYNTHETIC "IRON LAZULITE"*

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Abstract

Lipscombite, a synthetic iron phosphate mineral, was obtained both by the partial oxidation of ferrous phosphate and by the combination of suitable ferrous and ferric salts. It forms black, flat tetragonal bipyramids with a dark green streak. It has a defect structure with a variable number of Fe in its unit cell. The ferrous iron of lipscombite can be easily replaced by other divalent metals. No regular decrease in the unit cell size was detected with decreasing sizes of replacing ions. The replacement of ferric iron by aluminum takes place only partially, and with difficulty, resulting in isodimorphism. Another compound, ferrous ferric lazulite, monoclinic (?), with the formula $Fe^{++}Fe_2^{+++}(PO_4)_2(OH)_2$ was also synthesized.

Ferrous ferric lazulite changes to lipscombite between 110 and 290° C. Above 290° C. lipscombite contains no divalent iron. It changes to "iron berlinite" ($FePO_4$, quartz isotype) and hematite around 560° C., above which an unknown compound forms at the expense of both hematite and iron berlinite. If ferrous phosphate is only partially oxidized, lipscombite is obtained. However, if ferrous phosphate is heated in air, it is dehydrated and oxidized to an amorphous ferric phosphate below 110° C. This product crystallizes at about 560° C. to hematite, a ferric orthophosphate (cristobalite isotype), and the unknown compound mentioned above. The ferric orthophosphate (cristobalite isotype) is converted to iron berlinite (quartz isotype) below 650° C. *X*-ray data for iron berlinite, ferrous ferric lazulite, and various compounds with lipscombite structure are given.

Introduction and Acknowledgments

During the investigation of the stability relations of iron oxides (Gheith, 1951), a black compound forming small shiny crystals was obtained as a result of contamination with phosphorus. Its *x*-ray powder pattern is similar but not quite identical to that of lazulite. The crystal structure of this "iron lazulite" was found by Katz and Lipscomb (1951) to be tetragonal.[2] Another compound, indistinguishable from the former on the basis of general appearance and qualitative analysis, was found to form under apparently identical conditions. Its *x*-ray powder pattern, however, corresponds practically line for line to that of lazulite and differs only in having spacings corresponding to a larger unit cell. This compound, probably monoclinic, changes to the tetragonal compound at elevated temperatures. The tetragonal "iron lazulite" is herewith named "lipscombite" (pronounced lips-kum-ite), after Professor William N. Lipscomb of the University of Minnesota. The monoclinic (?) compound will be referred to as "ferrous ferric lazulite."

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* Most of this study constitutes part of a thesis submitted by the writer to the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree.

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[2] "Iron lazulite" was the name used by Katz and Lipscomb. Most of the investigation was carried out before Pecora and Fahey announced their discovery of scorzalite, $Fe^{++}Al_2(PO_4)_2(OH)_2$, in 1949.

Professor J. W. Gruner was the first to obtain this material, note its resemblance to lazulite and suggest the name lipscombite for it. The writer is indebted to him for his guidance throughout this research and for his critical reading of the manuscript. He also wishes to thank Professor Lipscomb and Dr. Katz for helpful suggestions. Financial aid by the Wakfia Fahmia through the Egyptian Government is gratefully acknowledged.

Synthesis of Lipscombite and Ferrous Ferric Lazulite

Crystals of linear dimensions of the order of .1 mm. were prepared. They are black and shiny and gem-like in appearance. Some of them resemble slightly flattened bipyramids, almost octahedra, showing no twinning as far as can be determined from its external shape. Under the microscope the crystals are opaque, and most of them show square outlines.[3] The smallest crystals, however, and the thin edges of the larger crystals, appear very dark green in transmitted light, with only slight pleochroism. The extinction angle measured from a square edge is 45°. Accurate determination of the refractive indices was not possible, but they were found to be higher than 1.670 and lower than 1.80 in well crystallized lipscombite containing 12.33% FeO. The birefringence is strong.

Although lazulite ($MgAl_2(PO_4)_2(OH)_2$) and scorzalite (theoretically $Fe^{++}Al_2(PO_4)_2(OH)_2$), are known to be monoclinic, Katz and Lipscomb (1951) showed that lipscombite is tetragonal. Using Mo K radiation and the Weissenberg *x*-ray spectrometer they showed that the unit cell is body centered, group $D_4^{10}-I\,4_12$, $a=5.37$ Å, $c=12.81$ Å.

The methods of formation of lipscombite and ferrous ferric lazulite (Table 1) fall broadly within two classes. The first class is the partial oxidation of ferrous phosphate under controlled laboratory conditions. Heating of ferrous phosphate in air even at temperatures as low as 100° C. results in its oxidation and dehydration. The product of such treatment is a yellow amorphous ferric phosphate that shows no ferrous iron on chemical analysis. The second class comprises the complex combination and double decomposition of simpler compounds supplying the required elements. Table 1 shows 16 selected experiments from over 100 trials to prepare lipscombite under various laboratory conditions. It indicates that no prediction can be made as to whether the product will be lipscombite or ferrous ferric lazulite. Both substances apparently form under identical conditions.

To determine the effect of the composition of starting materials on the

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[3] These most probably are the flattened tetragonal bipyramids (103) lying on one of their faces.

TABLE 1. EXPERIMENTS ON THE FORMATION OF LIPSCOMBITE AND FERROUS FERRIC LAZULITE

Exp. No.	Starting Materials	Experimental Detail	Temp. ° C.	Press. lb./in.[2]	pH[1]	Duration	Product		Streak	
									Ridgway's	
							Form	% FeO	Name	No.
456	Fe'' phosph.+H_2O	Sealed tube	108	23	7	2 days	Beta*	14.62	Olivaceous black (3)	23'''' m
86	Fe'' phosph.+H_2O in CO_2 atmosphere[2]	Sealed tube	180	153	2	4 days	Alpha*	17.54	Dusky dull green	37''' m
99 B	Fe'' phosph., dry	Tightly packed in corked vial	105	—	—	1 day	Beta*	12.33	Dull greenish black (2)	33'''' m
458	Fe'' phosph.+H_2O+5 drops conc. H_2SO_4	Sealed tube	108	23	1	2 days	Beta*		Dusky bluish green	41'' m
461	Fe'' phosph.+H_2O+5 drops dil. NaOH	Sealed tube	108	23	9	2 days	Beta*		Olivaceous black (3)	23'''' m
12	Fe'' phosph.+artif. lepidocrocite (3:1) +H_2O	Sealed tube in bomb	188	183	7	2 days	Beta*		Deep slate green	33'''' k
64	Fe'' phosph.+artif. goethite+H_2O; in CO_2 atmosphere	Open tube in bomb	180	153	5[3]	14 days	Alpha*	17.53	Dusky olive green	25''' m
27	Fe'' phosph.+$Fe_2(SO_4)_3$ solution	Open tube in bomb	185	2000[4]	4	10 days	Beta*		Deep slate green	33'''' k
13	Powdered vivianite+artif. lepidocrocite+H_2O	Sealed tube in bomb	185	171	7	10 days	Beta*		Dull greenish black (1)	29'''' m
463	Fe''' phosph.+$FeSO_4$ (1:5)+H_2O	Sealed tube	108	23	4	2 days	Beta[5]*		Dull blackish green	29''' m
145	Fe''' phosph.+$FeSO_4$ (6:1)+H_2O	Open tube in bomb	170	132	5	2 days	Beta*		Light danube green	35'' k
82-1	Fe''' phosph.+$FeSO_4$ (2:1)+H_2O	Boil	100	—	5	20 min.	Beta[5]*	9.54	Bottle green	37' m
56	Fe''' phosph.+$FeSO_4$ (1:1)+H_2O	Boil	100	—	4	1 hour	Beta*	1.55	Antique green	33 m
52	Fe''' phosph.+$FeSO_4$ (1:6)+H_2O	Sealed tube in bomb	185	171	3	11 days	Alpha[5]*		Myrtle green	41 m
42	Fe''' phosph +$FeSO_4$ sol.+NaOH (in sealed tube)[6]	In bomb	180	153	10[3]	13 days	Alpha*	17.50	Dusky bluish green	41'' m
465	Fe''' phosph.+$FeSO_4$ (1:5)+H_2O	Sealed tube in bomb	180	153	3	3 days	Alpha*		Myrtle green	41 m

[1] pH of solution at beginning of experiment.

[2] A small amount of air entered the tube during sealing.

[3] This pH value is that of the solution at the end of the experiment

[4] A tank of medical nitrogen supplied the necessary pressure.

[5] A light colored phosphate with an unidentified powder pattern formed a crust on top of the lipscombite. Several unidentified patterns were kindly examined by Professor Frondel. They did not correspond to any of the phosphates on file at Harvard.

[6] Three NaOH pellets were placed in a separate small, thin walled tube. At 180° C. the bomb was shaken vigorously to break this tube

* Alpha indicates the monoclinic (?) ferrous ferric lazulite; beta indicates lipscombite.

formation temperature of lipscombite, a series of 9 experiments were performed in pyrex tubes. In each tube were placed 2.245 gm. of finely powdered ferric phosphate and 25 cc. of water, to which were added known amounts of ferrous sulfate. The tubes, one third full of air, were sealed and placed in an oven at constant temperature. If at the end of 2 days no change had taken place, the temperature was raised 2° C. and kept constant for the next 2 days. As soon as lipscombite formed in any of the tubes, it was taken out and the heating process continued for the remaining tubes. The formation of lipscombite can easily be detected by its dark bluish green color. The products were *x*-rayed and found to be lipscombite, sometimes with a small amount of an unidentified compound. The results as shown in Table 2 indicate that the higher the ratio of ferrous to ferric iron in the starting materials, the lower is the temperature of formation of lipscombite. Furthermore, the rate of change of this formation temperature is greater at lower concentrations of ferrous iron.

TABLE 2. EFFECT OF COMPOSITION ON FORMATION TEMPERATURE OF LIPSCOMBITE

Ratio $\frac{gm.\ FeSO_4\cdot 7H_2O}{gm.\ Fe'''\ Phosph.}$[1]	Lowest Temp. of Formation ° C.	Ratio $\frac{gm.\ FeSO_4\cdot 7H_2O}{gm.\ Fe'''\ Phosph.}$[1]	Lowest Temp. of Formation ° C.
0.122	—[2]	4.54	65
0.532	—[2]	5.23	63.5
1.216	—[2]	5.87	61.5
2.426	72	6.88	80 ?
3.64	67		

[1] Eimer and Amend's "precipitated pure insoluble ferric phosphate" was used. No definite formula can be given.

[2] The temperature was gradually raised from 72° C. to 135° C., but the product was a gray colored unknown phosphate and not lipscombite.

CHEMICAL ANALYSIS AND FORMULA OF LIPSCOMBITE AND FERROUS FERRIC LAZULITE

Chemical Analysis of Lipscombite

The crystal structure of lipscombite as determined by Katz and Lipscomb (1951) is a defect structure with the unit cell containing: 4P, 4 OH, 16 O, and "about 7Fe distributed randomly" in eight equivalent positions. Table 3 shows the chemical analysis of two samples prepared by two different methods (Table 1). The high H_2O percentage in the analysis is to be expected, as the material is an extremely fine powder, and cannot be heated at 110° C. for any length of time, as partial oxidation of the ferrous iron is liable to take place.[4] It was assumed in the calculations that the amount of phosphorus present represents $2P_2O_5$, i.e., 4P per unit cell. The other oxide ratios were calculated on this basis.

Of the 36 negative charges per unit cell (16 O and 4 OH), 20 are compensated by the 4P. The remaining 16 must be compensated by Fe. The positive charges due to iron were, therefore, calculated and adjusted to 16. From these the number of both Fe^{++} and Fe^{+++} per unit cell was obtained (Table 3, last column). To maintain the tetragonal symmetry it must be assumed that the vacant cation positions (2.61 in the first case and 2.23 in the second) are distributed statistically over the whole lattice.

TABLE 3. CHEMICAL ANALYSIS AND NUMBER OF IRON IONS PER UNIT CELL IN LIPSCOMBITE

	Weight %	Molecular Ratios	No. of Oxide Molecules	+Charges on Fe	Charges on Fe, Adjusted to 16	Metal Ions Per Unit Cell
			Experiment 56			
Fe_2O_3	54.86	.3430	2.660	15.960	15.689	5.23
FeO	1.55	.0216	.167	.314	.311	.16
P_2O_5	36.63	.2582	2.000			
H_2O+	6.01					
H_2O-	.03					
Total	99.08					
			Experiment 99 B			
Fe_2O_3	46.68	.2920	2.325	13.950	13.38	4.46
FeO	12.33	.1718	1.369	2.738	2.62	1.31
P_2O_5	35.62	.2508	2.000			
H_2O	5.53					
Total	100.16					

Analysis of Exp. 56 and Fe^{++} determination of Exp. 99 B are by Mr. Lee Peck. The rest is by the writer aided by Mr. S. Khalafallah, Univ. of Minnesota.

The 16 positive charges due to iron per unit cell can, theoretically, be supplied by as little as $5\frac{1}{3}$ Fe^{+++} or as much as $8Fe^{++}$ with no change in the x-ray powder pattern, but with the formula correspondingly changing from $Fe_8^{+++}(PO_4)_6(OH)_6$ to $Fe_4^{++}(PO_4)_2(OH)_2$. It was possible to prepare lipscombite with no ferrous iron at all. Its x-ray powder pattern (J 12,

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[4] In finely powdered samples it is sometimes impossible to get rid of all the nonessential water even by heating for a considerable length of time at 110° C. (Kolthoff and Sandell, p. 299).

Table 4. X-Ray Powder Data for Lipscombite and Ferrous Ferric Lazulite As Compared to Lazulite
(See Figure 2)
Unfiltered iron radiation. Radius of camera = 57.3 mm.

Lipscombite of Exp. 99 B (with 12.33% FeO)			Lipscombite of Exp. J 12 (with no FeO)		Ferrous ferric lazulite of Exp. 86 (17.54% FeO)		Ferrous ferric lazulite of Exp. 52		Lazulite* (Graves Mt.)	
hkl	*d* Å	*I*	*d* Å	*I*	*d* Å	*I*	*d* Å	*I*	*d* Å	*I*
101	4.864	1	4.885	1	6.296	f	6.404	f	6.16	w
	3.669	2.5	3.684	2.5	5.288	f	5.376	f		
	3.544	1	3.522	2	4.793	2	4.845	2.5	4.72	m
103	3.329	10+	3.329	10+	3.661	2	3.708	1.5	3.60	vvw
004	3.200	7	3.183	8	3.548	f				
	2.880	f	2.859	f	3.310	10+	3.332	10+	3.23	s (b)
200	2.616	2	2.584	3	3.212	5	3.257	5	3.14	m
	2.544	f	2.507	f	3.157	4	3.186	5	3.07	m
202	2.422	1	2.276	3	2.882	f	2.908	f		
	2.299	2.5	2.239	1			2.665	f		
	2.267	f	2.035	5	2.612	2.5	2.618	3	2.55	m
213	2.056	5.5	1.872	1.5	2.413	1 b	2.431	1	2.34	vw
	2.036	1.5	1.825	2	2.325	4	2.329	4	2.26	w
	1.862	1	1.754	1.5	2.290	1.5	2.290	1.5	2.22	w
	1.845	2	1.665	4	2.053	4	2.117	f	2.05	vw
	1.773	1	1.631	f	2.028	3	2.063	3.5	2.01	w
017	1.747	1	1.589	5.5 b	1.859	2.5 b	2.031	2	1.977	mw (b)
206	1.664	5	1.451	1	1.833	1	1.867	1.5		
008	1.604	6 b	1.421	1	1.778	1	1.831	1	1.807	w
	1.449	1.5	1.379	f	1.754	1	1.788	f	1.787	vw
	1.441	1	1.358	f	1.727	f	1.752	f	1.684	vw
	1.374	1	1.305	1	1.680	4	1.684	4.5	1.618	w
			1.289	2	1.659	4	1.663	4.5	1.600	w
			1.227	1.5	1.613	5.5 b	1.614	6 b	1.568	m (b)
			1.202	1.5 b	1.587	1	1.589	1.5	1.538	w
					1.458	1	1.481	f	1.407	w
					1.441	1	1.465	1	1.389	vw
					1.389	1	1.442	1	1.274	m
					1.374	f	1.391	f	1.185	vw
					1.356	f	1.376	f	1.113	vvw
					1.306	5	1.354	f		
							1.308	5.5		

* The *x*-ray data for lazulite are after Pecora and Fahey (1950, p. 11); filtered Cu radiation.

b = broad, f = faint.

Table 4) shows minor differences from that of lipscombite containing both ferrous and ferric iron. The product forms small olive yellow crystals (Ridgway 23″) with a primrose yellow streak (23″ *d*). The light color suggests the absence of Fe in two different valence states. Under the microscope the small crystals have square outlines and very high relief, the refractive indices being higher than 1.83. With the nicols crossed the material shows beautiful abnormal interference colors, and no extinction. Trials to prepare the other end member, namely lipscombite with $8Fe^{++}$ and no Fe^{+++} in the unit cell were not successful.

Theoretical and Observed Densities of Lipscombite

The density of finely crystallized lipscombite cannot be determined accurately since it cannot be freed from water without partial oxidation. Katz and Lipscomb, however, determined the density of a rather coarsely crystalline sample. Using a sink or float method in a thalium malonate-thalium formate solution they found the density to be 3.8.

TABLE 5. VARIATION OF THE CALCULATED DENSITY OF LIPSCOMBITE WITH INCREASING FERROUS IRON CONTENT

Total No. of Fe per Unit Cell	No. of Fe^{++} per Unit Cell	No. of Fe^{+++} per Unit Cell	% Ratio Fe^{++}:Total Fe	Calculated Density
5½	½	5	9.09	3.395
6	2	4	33.33	3.520
6½	3½	3	53.85	3.646
7	5	2	71.43	3.771
7½	6½	1	92.86	3.897

Based on the dimensions of unit cells of several samples, the writer obtained the theoretical densities shown in Table 5. These represent density changes with variation in ferrous iron content. The relation between the density and the ratio of ferrous to total iron follows very nearly a straight line (Fig. 1). If well crystallized samples whose densities can be determined accurately are found in nature, Fig. 1 can be used to determine their approximate composition. As an example, the synthetic lipscombite sample with a density of 3.8 (Katz and Lipscomb, 1951) is seen from the figure to have a ferrous to total iron ratio of 77.8%.[5]

[5] As iron supplies 16 positive charges per unit cell, therefore:

$$K(77.8\times 2+22.2\times 3)=16$$

$$K=\frac{16}{(77.8\times 2+22.2\times 3)}=0.72$$

No. of Fe^{++} per unit cell $=77.8\times .072=5.60$

No. of Fe^{+++} per unit cell $=22.2\times .072=1.60$

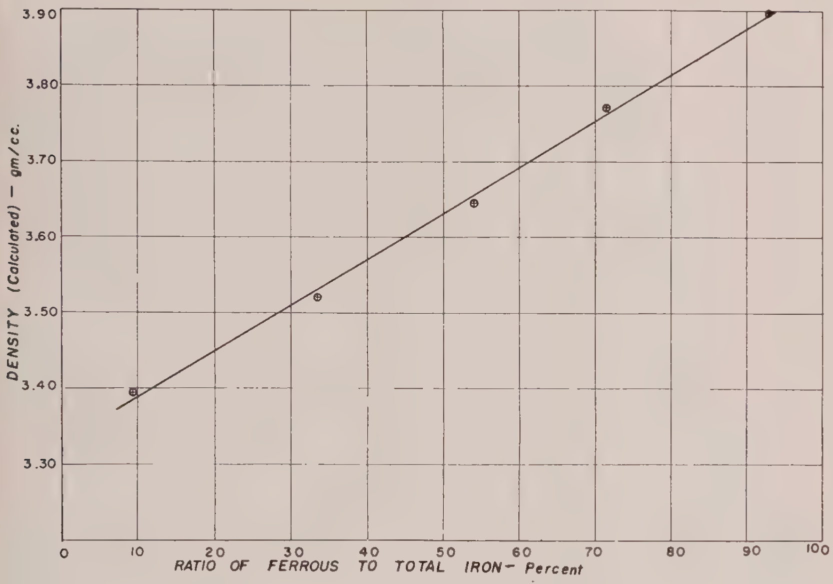

FIG. 1. Variation of the density of lipscombite with increasing ferrous iron content.

Chemical Composition of Ferrous Ferric Lazulite

The ferrous iron content of ferrous ferric lazulite shows only very limited variations as contrasted to that of lipscombite. Three ferrous ferric lazulite samples gave the values shown in Table 6.

TABLE 6. FERROUS AND FERRIC IRON CONTENT OF FERROUS FERRIC LAZULITE

	Exp. No. 42	Exp. No. 64	Exp. No. 86
FeO*	17.50	17.53	17.54
Fe_2O_3*	Not determined	42.74	41.82

* Ferrous iron determinations were made by Mr. Lee Peck; ferric iron by the writer.

A complete chemical analysis of ferrous ferric lazulite was not possible. As it gives an *x*-ray powder pattern very similar to that of lazulite and scorzalite $(Mg, Fe^{++})Al_2(PO_4)_2(OH)_2$, the theoretical chemical analysis

TABLE 7. CALCULATED CHEMICAL ANALYSIS OF $Fe^{++}Fe_2^{+++}(PO_4)_2(OH)_2$

Fe_2O_3	FeO	P_2O_5	H_2O+
40.79	18.35	36.26	4.60

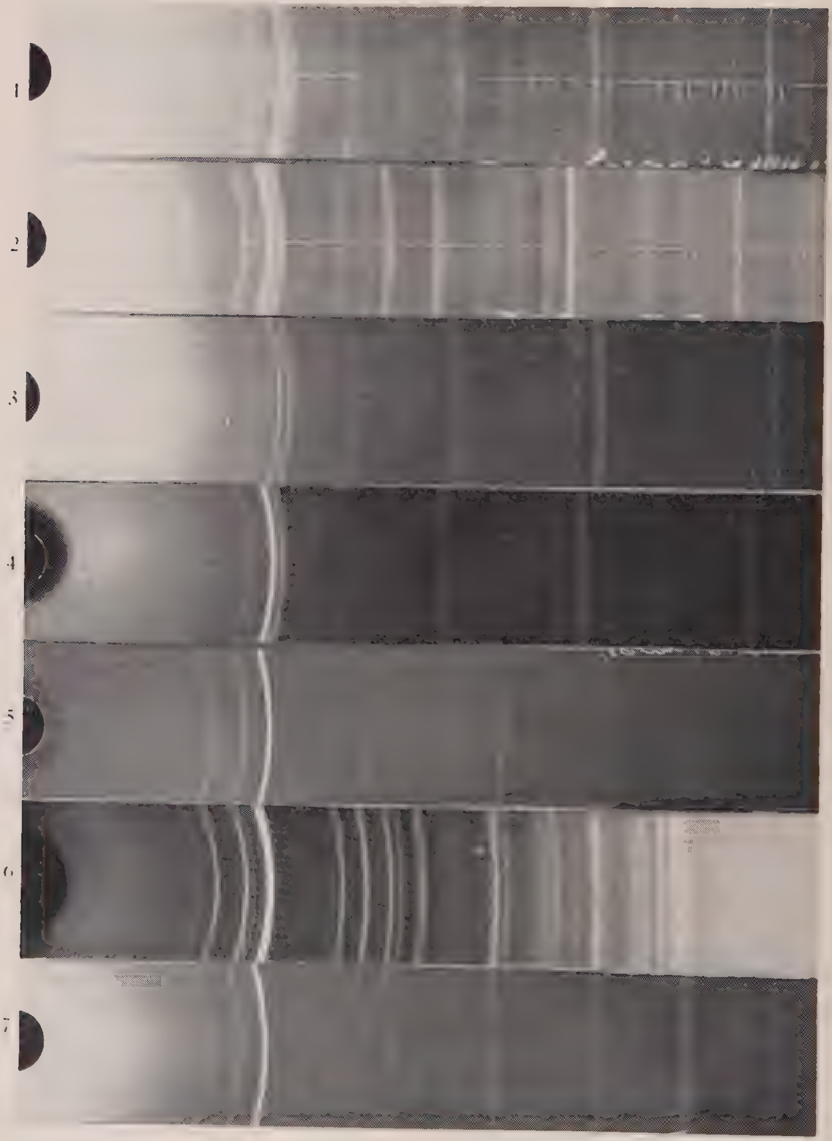

FIG. 2. Powder photographs (unfiltered iron radiation, radius of camera = 57.3 mm.) *From top to bottom:* 1. Lazulite; Matterhorn, Switzerland. 2. Ferrous ferric lazulite. 3. U. S. National Museum sample R5611 (supposed berlinite). 4. Lipscombite. 5. Quartz; natural. 6. Iron berlinite, lines not agreeing with berlinite are hematite lines. 7. Berlinite; synthetic.

for an iron lazulite with the formula $Fe^{++}Fe_2^{+++}(PO_4)_2(OH)_2$ was calculated and is given in Table 7. This formula most probably represents the composition of ferrous ferric lazulite.

HEAT TREATMENT OF LIPSCOMBITE AND FERROUS FERRIC LAZULITE

Differential thermal analysis did not yield any satisfactory reproducible results when applied to these synthetic iron phosphates. It was therefore decided to heat various samples at constant temperatures. Five samples were chosen, including ferrous phosphate (Eimer and Amend), two ferrous ferric lazulite and two lipscombite samples, each prepared by a different method (Table 1). Each sample was heated in a loosely covered crucible at a given temperature for three days. A small amount was then removed for *x*-raying and the rest of the sample heated at a higher temperature for the next three days. This treatment covered the range from 110° C. to 1000° C., but no changes occurred above 735° C.

The results as shown in Table 8 indicate that ferrous ferric lazulite changes to lipscombite between 110 and 290° C. This transition is rather sluggish, and is always accompanied by the oxidation of ferrous iron. The lipscombite structure, which contains only trivalent iron at temperatures higher than 290° C., seems to be stable up to about 560° C. At this temperature or slightly below it, a transformation of lipscombite to a phosphate, $FePO_4$, with a quartz-like structure, and to hematite proceeds slowly. As berlinite is $AlPO_4$ with a quartz structure, the corresponding $FePO_4$ is here named "iron berlinite." The *x*-ray powder data for this product are given in Table 12 and in Fig. 2. In the unit cell of lipscombite the minimum ratio of the number of Fe to P is $5\frac{1}{3}:4$. This means there is always an excess Fe over P above the ratio needed for the formation of $FePO_4$. Hematite and iron berlinite, therefore separate simultaneously upon heating lipscombite.

Table 8 also shows that at about 650° C., or higher, a compound with an unidentified structure coexists with iron berlinite and hematite. This compound is referred to as unknown "A".[6] From the progressive changes in the colors of the products along with the approximate determination of the relative amounts of the components as seen in the *x*-ray photographs, this unknown "A" seems to form at the expense of both hematite and iron berlinite.

Heating of ferrous phosphate in air yields an *amorphous* ferric phos-

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[6] It is significant to mention here that a sample of powdered vivianite, $Fe_3P_2O_8 \cdot 8H_2O$, heated at 1000° C., gave an *x*-ray photograph showing iron berlinite, unknown "A" and very little hematite. These are exactly the same products obtained by heating any of the samples of Table 8 above 735° C.

TABLE 8. THE HEAT TREATMENT OF LIPSCOMBITE, FERROUS PHOSPHATE AND FERROUS FERRIC LAZULITE

A.—UP TO 425° C.

Starting Material	110° C.		290° C.		359° C.		425° C.	
	Color	*X*-ray	Color	*X*-ray	Color	*X*-ray	Color	*X*-ray
Ferrous ferric lazulite of Exp. 86	Dark bluish green	Ferrous ferric lazulite	Dark olive yellow	Lipscombite	Dark olive yellow	Lipscombite[1]	Dark olive yellow	Lipscombite[1]
Ferrous ferric lazulite of Exp. 64	Dark green	Ferrous ferric lazulite	Yellowish brown	Lipscombite	Light brown	Lipscombite[1]	Orange brown	Lipscombite[1]
Ferrous phosphate (Eimer and Amend)	Yellow	Amorphous	Orange yellow	Amorphous	Yellowish brown	Amorphous	Yellowish brown	Amorphous
Lipscombite of Exp. 99 B	Greenish black	Lipscombite	Olive brown	Lipscombite	Brown	Lipscombite, v. sharp pattern	Brown	Lipscombite
Lipscombite of Exp. 82-1	Green	Lipscombite	Yellow	Lipscombite	Orange yellow	Lipscombite	Dark orange	Lipscombite

[1] Product has one extra line at $d = 6.520$ with $I = 1$ to 1.5.

TABLE 8—(*continued*)

B.—UP TO 1000° C.

Starting Material	560° C.		650° C.		735° C.	
	Color	*X*-ray	Color	*X*-ray	Color	*X*-ray
Ferrous ferric lazulite of Exp. 86	Dark brown	Lipscombite; Iron berlinite, v. faint	Dark brown	Lipscombite, v. faint; Iron berlinite; Unknown "A";[1] Hematite, v. little	Reddish buff	Iron berlinite; Unknown "A"; Hematite, v. little
Ferrous ferric lazulite of Exp. 64	Dark brown	Lipscombite	Dark reddish brown	Lipscombite; Iron berlinite; Hematite	Red	Iron berlinite; Unknown "A"; Hematite
Ferrous phosphate (Eimer and Amend)	Dark brown	Ferric orthophosphate (cristobalite isotype); Unknown "A"; Hematite, little	Light brown	Iron berlinite; Unknown "A"; Hematite, v. little	Light brown	Iron berlinite; Unknown "A"; Hematite, v. little
Lipscombite of Exp. 99 B	V. dark brown	Lipscombite; Iron berlinite; Hematite, little	Deep red	Iron berlinite; Hematite; Unknown "A"; v.v. little	Reddish buff	Iron berlinite; Unknown "A"; Hematite, v. little
Lipscombite of Exp. 82-1	Deep red	Lipscombite; v. faint; Iron berlinite; Hematite, faint	Red	Iron berlinite; Hematite; Unknown "A"; v.v. little	Reddish buff	Iron berlinite; Unknown "A"; Hematite, v. little

[1] Unknown "A" was always obtained with hematite and/or iron berlinite. This unknown has the following *x*-ray data:

d Å:	3.09	2.45	2.08	2.01	1.63
I :	10+	2	3.5	3	5

phate even below 110° C. At about 560° C. this amorphous product crystallizes to an iron phosphate with a cristobalite structure. The excess iron forms hematite or combines in part with some phosphorus to form the unknown "A". Between 560 and 650 °C. this ferric orthophosphate—$FePO_4$ (cristobalite isotype) undergoes a complete transformation to iron berlinite.

It is to be noted that ferric orthophosphate (cristobalite isotype) formed only from the crystallization of the amorphous ferric phosphate. When no amorphous intermediate product forms, the phosphate with a cristobalite structure is not obtained. A striking analogy can be drawn between these transformations and those among corresponding modifications of silica. Sosman (1927, p. 105) states that silica *glass* when heated below 870° C. with fluxes or "mineralizers," converts first to one of the unstable forms (here ferric orthophosphate (cristobalite isotype)) and later changes further to quartz (here iron berlinite).

Oxidation of Ferrous Iron in Lipscombite and Ferrous Ferric Lazulite

Table 8 shows that the oxidation of ferrous iron in lipscombite is apparently not accompanied by any structural changes discernible in an *x*-ray powder photograph. This oxidation, therefore, must take place without the addition of any oxygen, but rather by removing the H ions of the OH groups. Such a process was proposed by Starke (1939) in connection with the oxidation of synthetic magnetite.[7]

TABLE 9. VARIATION OF IRON CONTENT OF FERROUS FERRIC LAZULITE UPON HEATING

	At Room Temp.	Heated at 290° C.	Heated at 425° C.
X-ray data	Ferrous Ferric Lazulite	Lipscombite	Lipscombite
FeO	17.54	0.2?	0.00
Fe_2O_3	41.95	61.26	61.63
Total iron as Fe	43.02	42.99	43.10

The ferrous ferric lazulite is the product of Exp. 86. FeO determinations made by Mr. Lee Peck; Fe_2O_3 by the writer.

The oxidation of the ferrous iron of ferrous ferric lazulite on the other hand, is accompanied by a slight rearrangement of the structure resulting in lipscombite. Depending on *x*-ray evidence alone it cannot be said with certainty whether oxygen is added or H removed from the OH groups. Determination of ferrous and ferric iron content of the original and the oxidized products (Table 9), does not at first sight seem to solve the problem. When the weight per cent of FeO and Fe_2O_3 was recalculated as weight per cent of Fe, it was clearly seen that no oxygen was added during the oxidation. Any addition of oxygen should have resulted in a corresponding decrease of the percentage of Fe.

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[7] Frondel (1949) found that a similar process of oxidation takes place in rockbridgeite $Fe^{++}Fe_6^{+++}(PO_4)_4(OH)_8$, laubmannite $Fe_3^{++}Fe_6^{+++}(PO_4)_4(OH)_{12}$ and dufrenite $Fe^{++}Fe_4^{+++}(PO_4)_3(OH)_5 \cdot 2H_2O$.

ISOMORPHOUS SUBSTITUTION IN LIPSCOMBITE

Replacement of Iron by Divalent Metals

Lipscombite can be easily synthesized by heating powdered ferric phosphate in a ferrous sulfate solution (Table 1). If, however, other divalent metal sulfates are used, and the experiment performed in sealed tubes, or in bombs at temperatures usually higher than those required when ferrous sulfate is used, the lipscombite produced has a relatively light color (Table 10). This indicates that other divalent ions have replaced Fe^{++} ions, for almost without exception, crystals containing a given element in two different valence states are dark in color. *X*-ray data for magnesian lipscombite (of Exp. 58–1) are given in Table 12. Nickelian lipscombite (of Exp. 59) gave an identical powder pattern. Replacement of Fe^{++} by other divalent metals of various ionic radii does not result in any regular changes in the unit cell size.

TABLE 10. REPLACEMENT OF IRON BY DIVALENT METALS IN LIPSCOMBITE[1]

Exp. No.	Starting Materials	Experimental Detail	Temp. ° C.	Duration	Streak	
					Ridgway's	
					Name	No.
57-C	Ferric phosphate+$CoSO_4$ solution	Boil	100	3 hours	Raw sienna	17 i
58-4	Ferric phosphate+$MnSO_4$ solution	Sealed tube in bomb	180	7 days	Cream color	19′ f
58-1	Ferric phosphate+$MgSO_4$ solution	Sealed tube in bomb	180	7 days	Pale green-yellow	27 f
58-2	Ferric phosphate+$MgSO_4$ solution (10 cc.)+$FeSO_4$ solution (2 cc.)	Sealed tube in bomb	180	7 days	Niagara green	41″ b
58-3	Ferric phosphate+$MgH_4(PO_4)_2$ +water	Sealed tube in bomb	180	7 days	Pale green-yellow	27 f
59	Ferric phosphate+$NiSO_4$ solution	Sealed tube in bomb	180	1 day	Citron green	25″ b
66-3	Ferrous phosphate+$NiSO_4$ solution	Sealed tube in bomb	180	22 days	Civette green	31′ k

[1] All products were *x*-rayed and found to have a lipscombite structure.

Replacement of Iron by Aluminum

Over 40 experiments were performed in an attempt to synthesize lazulite, scorzalite, and the aluminian and chromian analogues of lipscombite. The products in most cases were berlinite and/or some unidentified compounds. Four experiments, however, yielded a product with lipscombite structure. The fact that *x*-ray data (Table 12) show a smaller unit cell than lipscombite containing iron alone, and that iron and aluminum are the only metal ions present in the starting materials (Exp. 69, Table 11), indicate that aluminum has, at least partially, replaced iron.[8] A chemical analysis is not possible, as this product always has either berlinite or a compound with an alunite structure mixed with it (Table 11).

TABLE 11. REPLACEMENT OF Fe^{+++} BY Al^{+++} IN LIPSCOMBITE

Exp. No.	Starting Materials	Experimental Detail	Temp. ° C.	Duration	Products	
					Color	*X*-Ray Data
67 A	$Al_2(SO_4)_3(NH_4)_2SO_4\cdot 24H_2O$ $+Fe^{++}$ phosphate $+H_2O$	Sealed tube in bomb	180	21 days	V. light green	Lipscombite: with smaller unit cell than that containing iron alone Compound with alunite structure
68 A	$Al_2(SO_4)_3(NH_4)_2SO_4\cdot 24H_2O$ $+Fe^{++}$ phosphate $+7$ drops $H_3PO_4+H_2O$	Sealed tube in bomb	180	12 days	Light pistachio green	Lipscombite: as in 67 A Berlinite
69	$Al_2(SO_4)_3\cdot 18H_2O+Fe^{++}$ phosphate $+H_2O$	Sealed tube in bomb	180	21 days	Pistachio green	Lipscombite: with smaller unit cell (measured, Table 12) Compound with alunite structure
75	Al phosphate $+Fe_2(SO_4)_3$ $+H_2O$ (all trivalent ions)	Sealed tube in bomb	180	12 days	Cream color	Lipscombite: with smaller unit cell, v. small amount Berlinite

A Mineral with a Structure Similar to Lipscombite

An *x*-ray powder photograph of the U. S. National Museum sample No. R5611 showed a structure very similar to that of lipscombite (Fig. 2, and Table 12). The sample was labelled berlinite, Westana, Sweden. This mineral, however, is biaxial and contains aluminum. It has the following properties: Color, very light greenish white to almost colorless. Luster vitreous. Hardness about 7. Refractive indices for yellow light: $\alpha=1.627\pm.002$, $\beta=1.643\pm.002$, $\gamma=1.648\pm.002$. Birefringence moderate to weak ($\gamma-\alpha=.021$). Optically negative. $2V=40°$ (calculated), moder-

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[8] The difficulty of the replacement of Al by Fe^{+++} in the lazulite-scorzalite series is pointed out by the fact that none of the ten samples examined by Pecora and Fahey had over 0.9% Fe_2O_3 (Dr. W. T. Pecora, personal correspondence, 1949).

TABLE 12. X-RAY DATA FOR IRON BERLINITE, TWO SYNTHETIC AND ONE NATURAL COMPOUNDS WITH LIPSCOMBITE STRUCTURE

(Unfiltered iron radiation. Radius of camera = 57.3 mm.)
(See Fig. 2)

Iron berlinite		Magnesian Lipscombite of Exp. 58-1		Al-containing lipscombite (+faint alunite structure) of Exp. 69		U.S.N.M. No. R5611 Supposed berlinite Westana, Sweden	
d Å	*I*	*d* Å	*I*	*d* Å	*I*	*d* Å	*I*
4.887	1	5.155	f	5.508	2[1]	5.018	f
4.422	6	3.726	3.5	3.600	1.5	4.627	.5
3.844	5	3.570	1.5	3.452	1.5[2]	3.515	2
3.471	10+	3.349	10+	3.362	f[3]	3.408	1.5
2.789	3.5	3.212	8	3.254	10+	3.349	f
3.624	f	2.894	f	3.134	8	3.192	10+
2.529	5[4]	2.622	3.5	2.975	7[3]	3.074	9
2.379	5	2.551	f	2.546	3	2.778	1
2.312	2	2.303	3	2.481	f	2.512	5
2.192	3.5	2.264	f	2.256	2[3]	2.329	1
2.087	f	2.056	5	2.251	1.5	2.212	1
2.047	f	2.038	1.5	2.108	f	2.156	.5
1.886	4	1.878	1.5	2.012	5	2.106	1
1.729	2	1.843	3	1.989	2.5	1.985	5
1.701	1.5[4]	1.766	2 b	1.914	3[3]	1.953	4
1.588	3	1.673	4	1.841	1	1.790	3
1.511	f	1.600	5 b	1.807	1	1.778	1
1.427	4 b	1.456	1.5	1.758	1[3]	1.710	1
1.412	f	1.435	1	1.727	f	1.679	1.5
1.341	1	1.384	f	1.636	5	1.608	3.5
1.295	f	1.372	f	1.569	6 b	1.597	2.5
1.243	f	1.341	1	1.518	f	1.548	6.5 b
1.232	f	1.301	3	1.494	2.5 b[3]	1.536	3
1.215	f	1.233	1	1.426	1.5	1.468	.5
		1.211	1	1.410	f	1.392	2.5 b
				1.393	f	1.328	1.5
				1.357	f	1.297	f
				1.332	f	1.268	1.5
				1.287	2	1.260	6
				1.277	2		

[1] Probably common to both alunite and aluminum-containing lipscombite.

[2] Common to both alunite and aluminum-containing lipscombite.

[3] Alunite reflection.

[4] Common to both iron berlinite and hematite.

ate as observed in comparison to muscovite. No pleochroism. This mineral can be easily distinguished from lazulite and scorzalite by its lighter color, weaker birefringence, smaller optic angle and absence of pleochroism.

Some Theoretical Considerations

The lipscombite series presents a complicated case of isomorphism in which definite chemical names indicating definite formulas cannot be given. It is believed that the presence of Al in place of Fe above a cerain ratio results in a monoclinic rather than a tetragonal compound. Furthermore the "lipscombite series" ranging from the tetragonal magnesium ferric phosphate to the tetragonal ferrous ferric phosphate, is itself isomorphous with the lazulite-scorzalite series through partial replacement of ferric iron by aluminum, i.e., we have a case of isodimorphism.

The problem becomes even more interesting when the unit cell constants for lipscombite are recalculated. Instead of taking the tetragonal unit cell of lipscombite (Katz and Lipscomb, 1951), a unit cell with the same orientation as Berry's (1948) new unit cell of lazulite is used. The results are:

	a_0	b_0	c_0	β
Lipscombite	7.002	7.593	7.002	114°31′
Lazulite	7.12	7.24	7.10	118°55′
Scorzalite	7.15	7.32	7.14	119°00′

Again if the conventional orientation of the monoclinic prismatic so-called orthogonal pseudohexagonal morphological cell is used (Dana, *System of Mineralogy*, 1952), the following constants are obtained:

Lipscombite	$a:b:c$	1:1:1.687	β	90°
Lazulite	$a:b:c$	.9750:1:1.6483	β	90°46′

Variations in the composition and properties of lipscombite as outlined in this paper may offer an explanation for some of the strange chemical analyses of "dufrenite-like" minerals, which do not afford a rational formula. Dufrenite itself has the formula $Fe''Fe'''_4(PO_4)_3(OH)_5 \cdot 2H_2O$ (Frondel, 1949).

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AFWILLITE FROM CRESTMORE, CALIFORNIA[1]

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Abstract

Afwillite, $3CaO \cdot 2SiO_2 \cdot 3H_2O$, has been found as crusts of small crystals along cracks in blocks of contact rock on the floor of the 910-foot level of the Commercial Quarry, Crestmore, near Riverside, California. Analysis gave: SiO_2 34.65, CaO 48.94, MgO trace, H_2O (+) 16.08, H_2O (−) 0.01, F=0.18, less O=F 0.10; total 99.76. Measurement of four crystals gave: $a:b:c=2.0712:1:2.3513$; $\beta=98°50'$. Crystals elongated parallel to [010], tabular parallel to {101}. The new forms {045}, {013}, $\{\bar{3}02\}$, $\{\bar{1}12\}$, {121}, {211}, $\{\bar{2}13\}$ $\{\bar{3}12\}$ were noted. Optically biaxial (+), 2V=55°, $\alpha=1.616$, $\beta=1.619$, $\gamma=1.631$, $X \wedge c=30°$. Cleavage {001} perfect, {100} good. Hardness 3. Specific gravity 2.62. Color white or colorless. *X*-ray powder data are given. Occurs with quartz and thaumasite on matrix of merwinite, gehlenite, and calcite.

Introduction

The marble, contact, and intrusive rocks at Crestmore, near Riverside, California, contain an unusually large variety of minerals. More than 100 different minerals have been identified from this area. Among the minerals is a series of hydrous calcium silicates—centrallassite, crestmoreite, hillebrandite, okenite, and riversideite.

A cross-section through the Commercial Quarry has been described in detail by Woodford, Crippen, and Garner (1941). Their paper lists all of the species then known to occur at Crestmore, as well as 14 additional unidentified species, tentatively designated by letters. A more recent summary of the geology and mineralogy of the Crestmore locality by Woodford (1943) gives more detailed information about these unidentified species. One of these unknowns, designated as *Mineral P*, has now been identified as afwillite, $3CaO \cdot 2SiO_2 \cdot 3H_2O$, another in the series of hydrous calcium silicates.

Afwillite was first described as a new species by Parry and Wright (1925). It was found in small quantity, associated with apophyllite, calcite, and natrolite, in a dolerite inclusion in kimberlite between the 500 and 750 foot levels of the Dutoitspan diamond mine, Kimberley, South Africa. A second occurrence was noted at Scawt Hill, Larne County, Antrim, Ireland, by Tilley (1930), where afwillite was found as small crystals with calcite in a spurrite rock. The Crestmore afwillite becomes the third known occurrence and the first in the Western Hemisphere.

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[1] Publication authorized by the Secretary, Smithsonian Institution, and the Director, U. S. Geological Survey.

The writers wish to thank Professor A. O. Woodford of Pomona College for the loan of specimens of Crestmore afwillite, and Mrs. Charlotte Warshaw of the U. S. Geological Survey for her two determinations of fluorine.

CHEMISTRY

A chemical analysis of afwillite from Crestmore is given in Table 1, along with one of the type material from Dutoitspan. The agreement between the analyses is good, and the Crestmore material is very close to the formula $3CaO \cdot 2SiO_2 \cdot 3H_2O$.[2]

TABLE 1. CHEMICAL ANALYSES OF AFWILLITE

	1	2	3	4
SiO_2	35.10	34.65	$0.577 = 2 \times 0.289$	35.13
R_2O_3	0.05	None		
CaO	49.00	48.94	$0.873 = 3 \times 0.291$	49.09
MgO	0.02	Trace		
$H_2O(+)$	15.81	16.08	$0.893 = 3 \times 0.298$	15.78
$H_2O(-)$	0.01	0.01		
F		0.18		
	99.99	99.86		100.00
Less O=F		0.10		
		99.76		

1. Afwillite from Dutoitspan mine, Kimberley, South Africa. H. S. Washington, analyst (Parry and Wright, 1925).
2. Afwillite from 910-foot level of the Commercial Quarry, Crestmore, San Bernardino County, California. G. Switzer, analyst. F determined by C. Warshaw (U.S.N.M. 105851).
3. Molecular ratios of analysis 2.
4. Theoretical composition for $3CaO \cdot 2SiO_2 \cdot 3H_2O$.

CRYSTALLOGRAPHY

The unit cell dimensions of afwillite from South Africa were determined by Gottfried (1933), who obtained the following results:

$a = 11.39$ kX
$b = 5.47$ kX
$c = 13.09$ kX
$\beta = 98°26'$ (from Parry and Wright, 1925)
$a:b:c = 2.08:1:2.39$

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[2] Recent work on the crystal structure of afwillite by Megaw (1949) shows that the silicon atoms occur in SiO_4 groups, each sharing one edge and two corners with the oxygen polyhedra surrounding neighboring calcium atoms, with some OH directly linked to silicon. The details of this work have not yet been published.

Gottfried found plates of afwillite cut perpendicular to the *b* axis to be distinctly piezoelectric, and hence assigned the mineral to the monoclinic-sphenoidal class (C_2). Etch tests made by Parry and Wright show no evidence of hemihedry, judging from their drawing of etch figures on (001).

X-ray powder photographs of type afwillite from South Africa and the Crestmore mineral are identical. The *d* spacings of the South African afwillite are given in Table 2 (heasurements by Switzer by photographic methods using a camera of 114.6 mm. diameter, intensities estimated visually).

TABLE 2. X-RAY POWDER DATA ON AFWILLITE FROM DUTOITSPAN MINE, KIMBERLEY, SOUTH AFRICA, COPPER RADIATION, NICKEL FILTER

No.	*I*	*d*	No.	*I*	*d*	No.	*I*	*d*
1	9	6.61	13	2	2.67	25	6	1.95
2	1	5.75	14	2	2.59	26	2	1.91
3	4	5.10	15	1	2.43	27	4	1.85
4	4	4.67	16	6	2.34	28	5	1.80
5	2	4.13	17	2	2.32	29	5	1.77
6	1	3.87	18	1	2.28	30	1	1.72
7	2	3.74	19	1	2.18	31	4	1.70
8	7	3.28	20	7	2.15	32	3	1.68
9	9	3.18	21	1	2.12	33	2	1.62
10	3	3.05	22	3	2.05	34	4	1.60
11	10	2.83	23	1	2.01	35	4	1.59
12	9	2.73	24	3	1.98	36	2	1.58

Afwillite from Crestmore is in part massive and in part crystallized. The crystals, which are colorless and transparent, range in length from less than 0.5 mm. to about 3 mm. They are well formed, with faces of a quality suitable for goniometry.

Table 3 gives a summary of the measurements obtained on four selected crystals from Crestmore, in the original setting of Parry and Wright (1925). The axial ratio in this setting, using measurements obtained on the Crestmore crystals, is $a:b:c=2.0712:1:2.3513$; $\beta=98°50'$. This ratio compares favorably with the figures obtained from *x*-ray measurements by Gottfried (1933) and is probably more precise than that determined by Parry and Wright (1925) on the Dutoitspan crystals, which were large and somewhat imperfect.

Of the forms listed in Table 3, the following are new: $\{045\}$, $\{013\}$, $\{\bar{3}02\}$, $\{\bar{1}12\}$, $\{121\}$, $\{211\}$, $\{\bar{2}13\}$ and $\{\bar{3}12\}$.

The appearance of a typical crystal is shown in Fig. 1. All the crystals are elongated parallel to [010], and most are tabular parallel to $\{101\}$.

Table 3. Measurement of Afwillite Crystals from Crestmore; (010) as Pole (in Setting of Parry and Wright, 1925)

	Number of		Quality	ϕ_2 from (001)	ρ_2	Range	
	Crystals	Faces				ϕ_2	ρ_2
001	4	6	E to P	0°00′	90°00′	0°00′ to 0°45′	89°40′ to 90°15′
100	4	5	G to P	98 50	90 00	98 30 to 99 05	89 36 to 90 21
110	4	7	E to P	98 50	26 02½	98 31 to 99 05	25 56 to 26 38
310	3	4	G	98 50	55 42	98 29 to 98 52	55 35 to 56 03
011	4	7	G to VP	0 00	23 18	0 00 to 4 08	23 08 to 24 13
045	1	1	G	0 00	28 17½	0 06	27 17
013	1	1	P	0 00	52 15	1 22	52 06
101	4	6	E to P	136 19	90 00	134 06 to 136 09	89 30 to 90 00
$\bar{1}01$	4	7	E to VP	53 39	90 00	52 54 to 54 00	90 00 to 90 32
$\bar{3}02$	1	1	P	66 18	90 00	63 36	90
$\bar{1}12$	4	5	G to VP	31 34	42 41	30 57 to 31 48	42 14 to 43 02
121	1	1	G	136 19	19 16	136 35	19 19
211	1	2	G	121 01	48 24½	119 19 to 121 05	48 16 to 48 24
$\bar{2}13$	3	3	F to VP	40 14	56 13	39 56 to 41 50	56 15 to 56 27
$\bar{3}12$	1	1	P	66 18	57 42	67 02	56 35

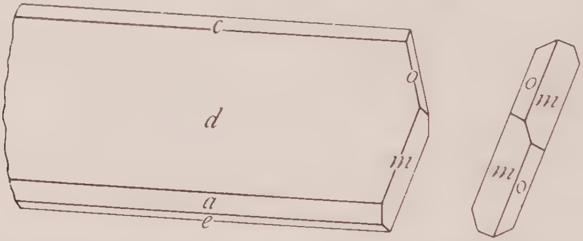

Fig. 1. Crestmore afwillite crystal showing typical habit: tabular parallel to *d*{101} and elongated parallel to [010]. Forms present are *c*{001}, *d*{101}, *a*{100}, *e*{$\bar{1}$01}, *o*{011}, and *m*{110}.

Physical Properties

The optical properties of afwillite from Crestmore are essentially the same as those reported for material from other localities. They are as follows:

$$\left.\begin{array}{l}\alpha=1.616\\ \beta=1.619\\ \gamma=1.631\end{array}\right\}\pm 0.002$$

Biaxial (+) 2V = 55° ± 3°

$Y=b$, $X\wedge c=30°$

Other properties are: {001} cleavage perfect, {100} cleavage good; H = 3; Sp. gr. = 2.62 ± 0.01.

Occurrence and Associations

Afwillite (*Mineral P*) was found in small quantity as thin crusts and crystals along cracks in loose blocks of contact rock on the floor of the

910-foot level of the Commercial Quarry. Associated with it are small crystals of quartz, as well as stout hexagonal prisms of thaumasite (referred to as *Mineral K* by Woodford, Crippen, and Garner, 1941).

The afwillite crusts and crystals occur on a matrix of granular, light-gray contact rock composed chiefly of merwinite, gehlenite, and calcite, with smaller amounts of spurrite, idocrase, monticellite, garnet, and brucite. This matrix has the typical appearance of the frequently occurring merwinite-gehlenite mixture of the locality.

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ALLOPHANES FROM LAWRENCE COUNTY, INDIANA

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Abstract

The properties of allophane from the South Gardner Mine, Lawrence County, Indiana, are presented. The optical properties indicate that the indices of refraction are a function of the adsorbed water. The differential thermal analyses suggest that the water above 100° C. is structurally held. The *x*-ray data indicate that allophane has a more ordered structure than glass. The base exchange is high and it is assumed that the base exchange capacity is due to unsatisfied bonds. Its bonding strength is low. Its soil mechanic properties would probably be similar to those of halloysite and its ceramic properties are light burning, high shrinkage, high P.C.E. value, and low plasticity.

Introduction

This report is concerned with the data obtained in analytical experiments with nearly pure allophane from the abandoned South Gardner Mine in sec. 28, T. 4 N., R. 2 W., Lawrence County, Indiana. The samples were collected in 1947 by the writer in the company of Dr. Eugene Callaghan, then of the Indiana Geological Survey, now Director of the New Mexico Bureau of Mines, and Dr. R. E. Grim and Dr. W. F. Bradley of the Illinois Geological Survey.

Allophane is the name applied to any amorphous substance which may be present in clay materials as extremely fine material and which has an indefinite composition. Since the allophanes vary in composition their characteristics may be expected to vary from sample to sample. Allophane has attracted little attention from clay students, probably because it is rarely found in the pure state and because its presence in soils and sediments is difficult to determine. Since there are so few data on allophanes available in the literature, it seems desirable to record information for these samples. Data for additional samples are needed before ranges of composition and properties of allophane are known. It must be remembered that the data which are derived from these samples may or may not be indicative of all other allophanes.

The allophanes in South Gardner mine are of two types: one is brittle, glassy, transparent, and blue; the other is granular and pink. As soon as the samples were collected, they were put into glass jars and sealed to prevent escape of moisture, and when brought to the laboratory a little distilled water was added to prevent any loss of water.

Optical Properties

The indices of refraction of the allophane samples were determined by the oil immersion method in oils which had been checked immediately preceding the analysis with a refractometer. Samples were used: (1) as they came from the mine, (2) after drying for two days in air, (3) after being heated at 100° C. and 140° C. over night, and (4) after being heated to 500° C. The indices were also determined on a sample of glassy allophane which had dried in air for a year.

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* Associate Geologist, Division of Clay Resources and Clay Mineral Technology, Illinois State Geological Survey.

The index of some of the particles of pink allophane (as taken from the mine) was first lower than that of the oil but when determined soon again was found to be above that of the oil. This is due either to the dehydration of the mineral and the adsorption of the moisture by the oil to lower the index of the oil or to the adsorption of the oil by the mineral.

Table 1. Optical Properties of the Allophanes from Lawrence County, Indiana

Treatment	H_2O*	Indices of refraction *n*
Pink allophane		
As from mine	34.69	1.398–1.423
Dried in air 48 hrs.	23.47	1.450–1.472
Heated at 100° C. over night	10.58	1.473–1.480
Heated at 140° C. over night	—	1.470–1.485
Heated up to 500° C. in 1 hr.	—	1.465–1.474
Glassy allophane		
As from mine	30.13	1.440–1.460
Dried in air 52 hrs.	25.68	1.461–1.474
Dried in air 1 yr.	20.11	1.480–1.486
Heated at 100° C. over night	11.82	1.487–1.494
Heated at 140° C. over night	—	1.484–1.494
Heated up to 500° C. in 1 hr.	—	1.465–1.482

* Water lost on drying to 140° C.

The indices of refraction of the allophane increased with the loss of water, as shown in Table 1. The material as taken from the mine had indices of refraction which varied widely ($N = 1.398$ to 1.460). After the allophane dried for 2 days the indices ranged from 1.450 to 1.474. The glassy allophane which had been dried for a year had an index range of 1.480 to 1.486, which was near the average value of 1.485 given by Ross and Kerr.[1] When samples were heated to 100° C. the indices ranged from 1.473 to 1.494; when heated to 140° C. the indices ranged from 1.470 to 1.494. After samples had been heated up to 500° C. the indices ranged from 1.465 to 1.482. The data in Table 1 indicate that the water driven off below 100° C. is an important factor in determining the index of refraction, but that driven off above 100° C. has little effect on the index.

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[1] Ross, C. S., and Kerr, P. F., Halloysite and allophane: *U. S. Geol. Survey Prof. Paper* **185G,** 135–148 (1934).

CHEMICAL DATA

The chemical analyses are given in Table 2.

TABLE 2. CHEMICAL ANALYSIS OF ALLOPHANES

	1	2
SiO_2	30.23	26.68
Al_2O_3	41.81	44.95
Fe_2O_3	0.31	0.12
MgO	0.04	none
CaO	2.86	2.37
P_2O_5	9.51	10.57
SO_3	0.44	0.22
Ign.	15.56	16.21
Total	100.81	101.30
H_2O-	34.69	30.13
H_2O+	15.61	16.39
$SiO_2:Al_2O_3$	1.23	1.01

1. Pink allophane, Lawrence County, Ind., analyzed by L. D. McVicker.
2. Glassy allophane, Lawrence County, Ind., analyzed by L. D. McVicker.

DIFFERENTIAL THERMAL ANALYSIS

Thermal analyses were run by the method and with the equipment used by Grim and Rowland.[2] A sample of each allophane as it came from the mine was heated to 1000° C. in the differential thermal furnace (Fig. 1*B* shows curves). Since there is a large amount of adsorbed water, the first endothermic reaction, which ranged from about 60° C. to 350° C., was large compared with that of other clays. Then fresh samples were heated over night in an oven to 110° C. and after cooling they were heated to 1100° C. in the differential thermal furnace (Fig. 1*A* shows curves). More energy was required to drive off the water from the preheated samples than from the unheated samples, as is shown by the fact that a temperature of from 475° to 500° C. was required to finish driving off all the water from the preheated sample. The endothermic reaction beginning about 500° C. is probably due to a trace of alunite, halloysite, or pseudowavellite. The exothermic reaction (between 1015 and 1085° C.) involves the formation of a new compound (mullite).

[2] Grim, R. E., and Rowland, R. A., Differential thermal analysis of clays and shales, a control and prospecting method: *Jour. Am. Ceram. Soc.*, **27**, 65–76 (1944), or *Illinois State Geol. Survey R. I.* **96** (1944).

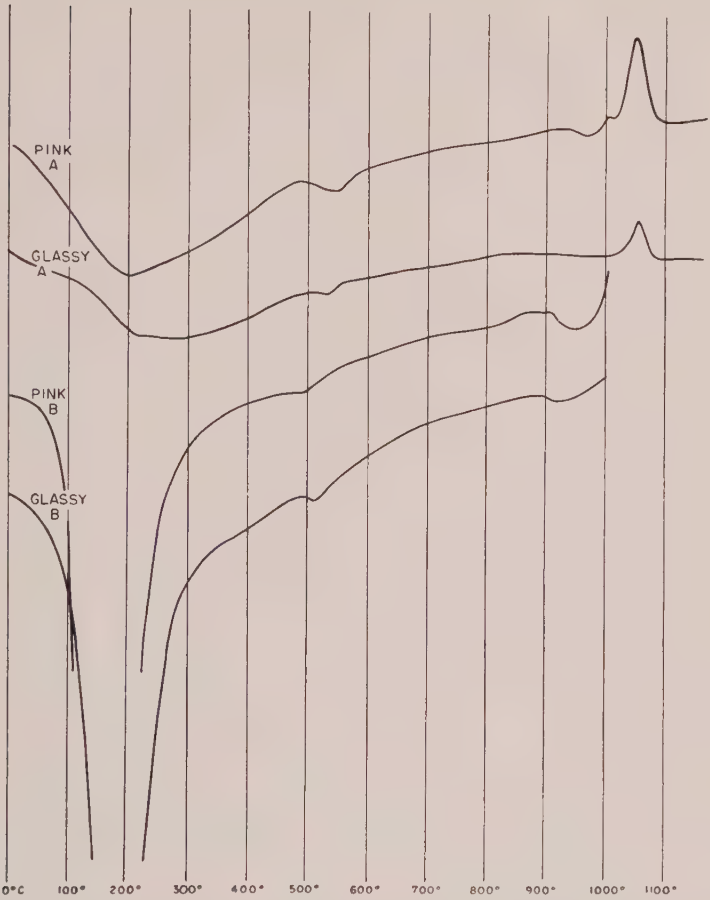
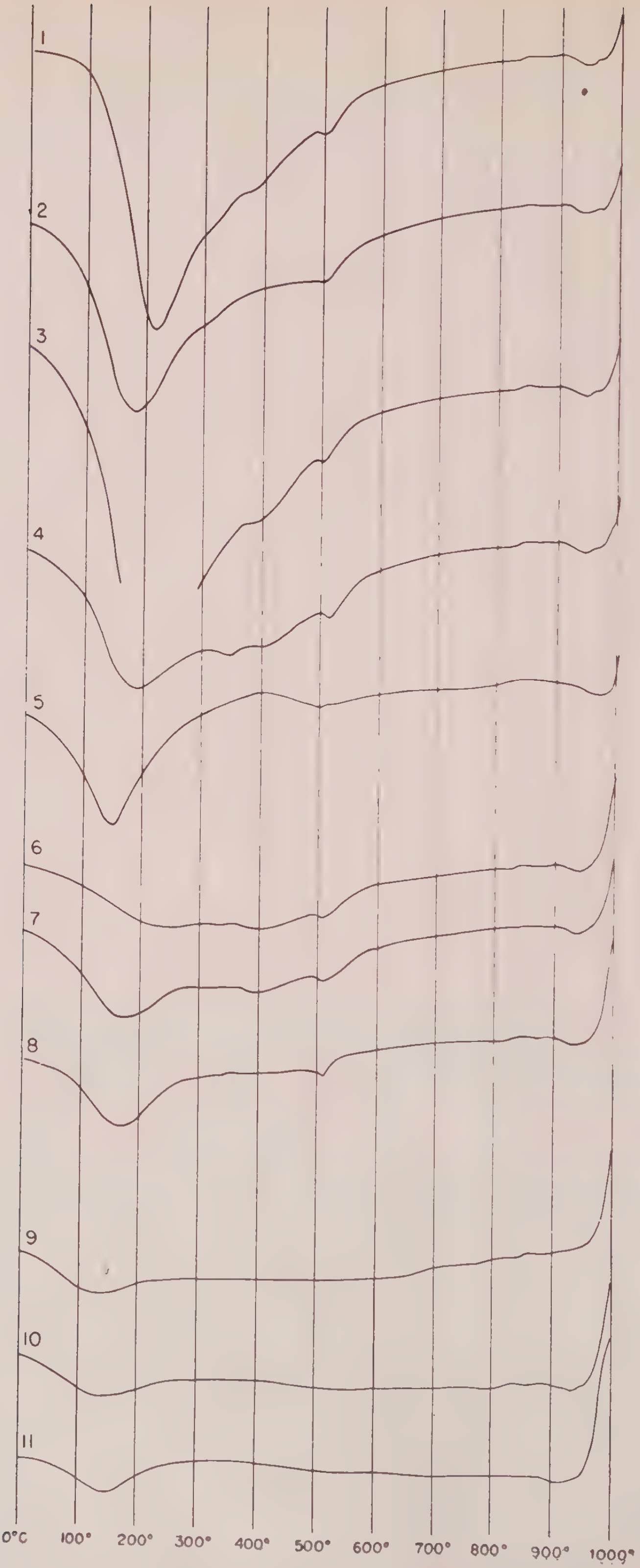


FIG. 1. Differential Thermalgram of Allophane. *A*. The allophanes were preheated at 140° C. over night before being heated in differential thermal furnace to 1100° C. *B*. The allophanes were heated in the differential thermal furnace as they came from the mine showing the large amount of adsorbed water.

DEHYDRATION AND REHYDRATION DATA

When allophane is heated to 100° C. most of the adsorbed water is driven off, but upon cooling, the water is readsorbed rapidly, as shown by the thermalgrams in Fig. 2. As allophane is heated to higher and higher temperatures, above 100° C., less and less water is readsorbed upon cooling, as shown by the thermalgrams in Fig. 2. This may indicate that allophane has some sort of open structure that can adsorb large quantities of water, but that, upon heating above 100° C., this porous network begins to collapse, owing to the fact that chemically


1
2
3
4
5
6
7
8
9
10
11
0°C
100°
200°
300°
400°
500°
600°
700°
800°
900°
1000°

combined water is being driven off. Upon cooling, probably very little, if any, water would be recombined chemically in the structure, and the amount of water that could be readsorbed by the collapsed structure would thus be reduced.

The thermalgrams suggest that almost all, if not all, the chemically combined water has been driven off below 500° C., and the water that is readsorbed is physically adsorbed for the most part.

X-RAY DATA[3]

The *x*-ray powder diffraction pattern for the glassy and pink allophanes showed four diffuse very broad bands, with traces of others, and faint diffraction lines which indicate a mineral with the alunite crystallization probably pseudowavellite. Ross and Kerr[1] reported one diffuse band and traces of others. As nearly as the four bands could be measured, the first ranged from 3.5 to 3.0 Å; the second, from 2.26 to 2.08 Å; the third from 1.45 to 1.27 Å; and the fourth, from 1.22 to 1.12 Å. This would indicate that allophane has a more ordered structure than glass.

The samples of allophane were heated to 750° and 1100° C., and *x*-ray patterns were taken. The diffraction pattern of the glassy allophane having been previously heated to 750° C. showed a few faint diffraction

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[3] I am indebted to W. F. Bradley of the Illinois State Geological Survey for the analysis and interpretation of the *x*-ray patterns.

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FIG. 2. Differential Thermal Analyses of Allophanes being Preheated at Various Temperatures.

1. Glassy allophane was run immediately after being heated to 100° C. over night.
2. Pink allophane was run after sitting in air 24 hours after being heated to 100° C. over night.
3. Glassy allophane was run after standing in air 60 hours after being heated to 100° C. over night.
4. Pink allophane was run after standing 12 hours in air after being heated to 200° C. over night.
5. Glassy allophane was run after standing 4 days in air after being heated to 200° C. over night.
6. Glassy allophane was run after standing 12 hours after being heated to 300° C. for 1 hour.
7. Glassy allophane was run after standing 4 days after being heated to 300° C. for 1 hour.
8. Glassy allophane was run after standing in air 80 days after being heated to 300° C. for 1 hour.
9. Glassy allophane was run after standing 24 hours after being heated to 500° C. for 1 hour.
10. Glassy allophane was run after standing in air 6 days after being heated to 500° C. for 1 hour.
11. Glassy allophane was run after standing 84 days in air after being heated to 500° C. for 1 hour.

lines in the position and characteristic of the stronger lines of a mullite diffraction diagram indicating that mullite probably had started to form, but the diffraction pattern of the pink allophane heated to the same temperature did not show any diffraction lines indicating that no new phases had started to form. Both allophanes showed complete conversion to mullite at 1100° C. (Fig. 3).[4]

BASE EXCHANGE CAPACITY

The base exchange capacity of allophane was determined by the ammonium acetate method used by Bray.[5] The base exchange capacity of the glassy and pink allophanes is 69.0 and 73.5 m.e. per 100 gm. respectively, which is high for clay minerals. This high exchange capacity is probably due to unsatisfied bonds, since the crystal structure is so poorly organized. In the crystalline clay minerals (Table 3) having a high exchange capacity, the capacity is due chiefly to substitutions in the lattice; whereas in the crystalline clay minerals having a low exchange capacity, the capacity is due chiefly to unsatisfied bonds on the edges of the lattice.

TABLE 3. BASE EXCHANGE CAPACITY FOR CLAY MINERALS

Clay Minerals	me/100 gm.	Nature of Exchange Bases
Montmorillonite[6]	60–100	Substitutions in lattice chiefly.
Allophane	69–73.5	Unsatisfied bonds.
Illite[6]	20–40	Substitution in lattice and unsatisfied bonds on edges of lattice.
Attapulgite[6]	20–30	Unsatisfied bonds on edges of lattice.
Kaolinite[6]	5–15	Unsatisfied bonds on edges of lattice.
Halloysite[6]	6–15	Unsatisfied bonds on edges of lattice.

[6] Grim, R. E., Modern concepts of clay materials: *Jour. Geol.*, 50, 225–275 (1942).

Since allophane and halloysite frequently occur together, this may explain the high base exchange capacities obtained by some students of clay mineralogy for halloysite.

BONDING STRENGTH

Clay-sand bonding strength tests for the pink and glassy allophanes were made by the standard procedure set up by the American Foundry-

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[4] Used with permission of W. F. Bradley.

[5] Bray, R. H., Base exchange procedure: *Dept. of Agron., Ag. Exper. Station, U. of Ill. Coll. of Ag.*, Urbana, Ill., Jan. 1942 (5 pp.).

[6] Footnote in Table 3.

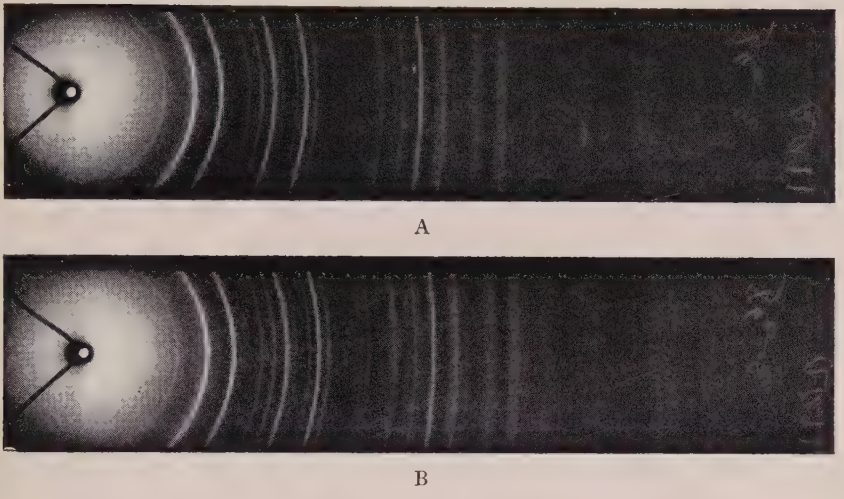

FIG. 3. *X*-ray Diffraction Patterns of Allophane heated to 1100° C.
A. Glassy allophane. *B*. Pink allophane.

men's Association.[7] The bonding strength for the allophanes was low compared with that of the crystalline clay minerals, as illustrated in Table 4.

TABLE 4. BONDING STRENGTH FOR CLAY MINERALS

	Clay per cent	Max. G.C.S.*
Kaolinite[8]	8	14.6
Illite[8]	8	12.7
Montmorillonite[8]		
Belle Fourche	8	24.1
Mississippian	8	30.5
Halloysite[8]	8	21.3
Attapulgite	8	7.4
Allophane	8	3.0

* Green Compression Strength.

[8] Grim, R. E., and Cuthbert, F. L., The bonding action of clays, Part I—Clays in green molding sands: *Illinois State Geol. Sur.*, *R. I.* 102, 55 pp. (1945).

OTHER PROPERTIES

By the standard method of Atterberg for determining plasticity, the Lawrence County, Indiana, allophanes are not plastic as they will not roll into a thread $\frac{1}{8}$ inch in diameter at any water content. The soil mechanic properties of these allophanes would in all probability be similar to those of halloysite.

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[7] Foundry Sand Testing Handbook, 1944 ed. Am. Foundrymen's Assoc., Chicago, Ill.

[8] Footenote in Table 4.

The shrinkage was high. When fired to 1000° C. in the differential thermal furnace, the total shrinkage was estimated to be about 50 per cent volume shrinkage.

The burning color was white.

Although the inability of the cone to stand the blast from the P.C.E. furnace prevented determination of the fusion point, the facts that the allophanes showed very little vitrification at 1200° C. and that they have a high alumina ratio suggest that the fusion point is probably high.

The specific gravity as given by Ford[9] for allophane is 1.85–1.89.

Manuscript received Aug. 22, 1952.

[9] Ford, W. E., Dana's Textbook of Mineralogy, 3rd Ed., John Wiley and Sons, Inc., New York (1922), p. 580.

REEXAMINATION OF THE CRYSTAL STRUCTURE OF MELILITE

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Abstract

An accurate single-crystal investigation of an intermediate melilite has confirmed the structure found by Warren in 1930. Variations in O—O distances are explained by sharing of polyhedron edges. Variations in Si—O distances are not explained by cation-cation repulsion. There is a considerable deviation from Pauling's rule of electrostatic valence bonds. This deviation may be related to the variation in Si—O distances since the longer the distance the larger is the sum of electrostatic valence bonds. The Ca polyhedron is a fairly regular square antiprism. The Ca—O distances are in two groups at 2.4 Å and 2.7 Å, suggesting that the bonds have different characters. A discussion of the possible arrangements of Mg, Al, and Si atoms in the melilite series is given. Consideration of some new analyses on natural melilites confirms the accepted melilite formula and disproves Goldsmith's hypothesis of the necessity for OH' replacing O'' in melilites.

Introduction

Melilite forms a continuous series between the end-members akermanite, $Ca_2MgSi_2O_7$, and gehlenite, $Ca_2Al_2SiO_7$. The composition of the natural melilites was extensively studied by Berman (1929) who found that the composition of the group could be well represented by $(Ca,Na)_2(Mg,Al,Si)_3O_7$ where (Ca,Na) is mainly Ca, $Mg<1.0$, and $Si<2.0$. Ferrous iron is also thought to substitute for the cations. Synthetic melilites have been produced in many experiments (see Goldsmith, 1948 for references), and their optical and morphological properties have been found to be similar to those of the natural melilites. Warren (1930) determined the crystal structure of a natural melilite from Capo di Bove, and Raaz (1930) determined the crystal structure of synthetic gehlenite. Apart from the necessary substitution of different cations, these structures are the same. The composition determined by Berman is confirmed by these two structure determinations. Andrews (1948) and Ervin and Osborn (1949) have independently measured the lattice parameters of the synthetic akermanite-gehlenite series and found regular changes throughout the whole series indicating complete solid solution. Warren and Trautz (1930) have shown that hardystonite, $Ca_2ZnSi_2O_7$, has the same structure as melilite.

It was thought that a redetermination of the melilite structure by the more accurate modern methods would be of interest for the following reasons: (*a*) the distribution of the Mg, Al, Si, atoms in the structure could be determined; (*b*) the coordination polyhedron of the Ca ion is variable in other crystals; (*c*) the possible distortion of the tetrahedra could be compared with the distortion found in the Si_2O_7 groups of tilleyite by Smith (1953*a*); and (*d*) the determination of accurate coordinates would provide a firm basis for the application of crystal-chemistry arguments to the possible substitutions in the melilites.

The natural melilite from Capo di Bove was chosen for analysis because Warren's crystals came from this locality.

PHYSICAL PROPERTIES AND COMPOSITION

The Capo di Bove melilite used in this work occurred as well crystallized tetragonal crystals showing only the (100) and (001) forms. The crystals were yellowish-brown and partly opaque. Some dark brown spots on the surface of the crystal indicated the presence of some impurity in small amounts; the main body of the crystal, however, was uniform.

Optical measurements, kindly carried out by W. S. MacKenzie of this Laboratory, gave: $\omega = 1.638 \pm 0.002$, $\epsilon = 1.634 \pm 0.002$, optically negative, $\omega - \epsilon = 0.004$.

Five analyses of Capo di Bove melilite have been made. These have been collected by Berman (1929) and are reproduced in Table 1. Analysis 2 differs considerably from the other four and it was provisionally disregarded. A mean of the other four was taken and when calculated to seven oxygen atoms the following formula was obtained:

TABLE 1. ANALYSES OF CAPO DI BOVE MELILITE

	I	II	III	IV	V
CaO	32.98	34.78	32.47	32.18	32.05
NaO	2.18	3.40	1.95	2.21	2.12
K_2O	1.49	0.68	1.46	1.45	1.51
MgO	6.33	5.87	6.44	6.41	6.71
Al_2O_3	6.47	10.93	6.42	7.56	8.61
SiO_2	40.14	41.09	39.27	39.20	38.34
Fe_2O_3	9.95	3.40	10.17	11.34	10.02
FeO	0.53	—	—	—	—

Analyses have been taken from Berman (1929).

$$Ca_{1.648}Na_{0.195}K_{0.089}Mg_{0.457}Al_{0.406}Si_{1.862}Fe_{0.417}O_7.$$

The assignment of atoms to the possible atomic sites in Warren's structure gave:

$[Ca_{1.648}Na_{0.195}K_{0.089}Fe_{0.068}]$	$[Mg_{0.457}Al_{0.268}Fe_{0.275}]$	$[Si_{1.862}Al_{0.138}]O_7$
Total 2 atoms	Total 1 atom	Total 2 atoms

with an excess of 0.084 atoms of Fe. The excess iron was a little disturbing; however, the crystal used in this work showed some brown impurities and a few weak extraneous reflections were observed on the Weissenberg photographs. It was thought that these impurities may have been some iron compound. The analysis was therefore recalculated neglecting iron oxide. The result was:

$[Ca_{1.752}Na_{0.207}K_{0.095}]$	$[Mg_{0.486}Al_{0.412}]$	$[Si_{1.980}Al_{0.020}]O_7$
Total 2.054 atoms	Total 0.898 atoms	Total 2 atoms

This also was unsatisfactory because the atomic sums are not integers. Later in the structure determination the composition was deduced from the x-ray measurements and from the refractive indices.

X-Ray Measurements

The crystals are tetragonal with $a=7.789\pm0.005$ Å, $c=5.018\pm0.005$ Å, determined by the θ method (Weisz, Cochran and Cole, 1948) using Co K_{α_1} and Co K_{α_2} radiation ($\lambda_{\alpha_1}=1.78890$ Å, $\lambda_{\alpha_2}=1.79279$ Å). The corresponding values obtained by Warren are 7.74 Å and 5.02 Å, when his values are converted from KX units into Å. The axial ratio c/a obtained in this work is 0.6442, which compares well with the goniometric axial ratio, 0.6440. This is obtained from that of Des Cloiseaux (1862) after reindexing the parametral plane. The space group is $P\bar{4}2_1m$ or $P42_1$ as the only systematic absences are for reflections with h odd in ($h00$). Warren discarded $P42_1$ as it was not possible to build a reasonable structure on this space group. There are two melilite units in the unit cell.

A crystal showing (001) and (100) faces was selected and cut with a razor-blade until it had a cross-section of 0.43×0.47 mm. perpendicular to the y-axis. The intensities of the ($h0l$) reflections were then recorded on multiple packs of film placed in a Weissenberg camera. MoK_α radiation was used and reflections were recorded from planes of spacing greater than 0.44 Å. The range of intensity was about 1500 to 1, and absorbing copper foil giving a step-down ratio of 3:1 from film to film was used. The intensities were measured visually by comparison with a calibrated intensity scale, and the Lorentz and polarization factors were applied by the method of Cochran (1948). As the crystal had a nearly uniform cross-section, no correction was made for differential absorption. The remaining correction factors (except for extinction) should be functions of sin θ and were found later in the structure determination. A rough correction for extinction was also made later in the structure determination.

Determination of the Atomic Coordinates

Structure amplitudes for the ($h0l$) reflections were calculated from the atomic coordinates given by Warren (these are given in Table 2). The space group $P\bar{4}2_1m$ is non-centrosymmetric; however, by a suitable choice

TABLE 2. ATOMIC COORDINATES DETERMINED BY WARREN

Atom	*x*	*y*	*z*
Ca	0.33	0.17	0.51
Si	0.14	0.36	0.95
Mg	0.00	0.00	0.00
O_1	0.50	0.00	0.19
O_2	0.14	0.36	0.26
O_3	0.08	0.18	0.81

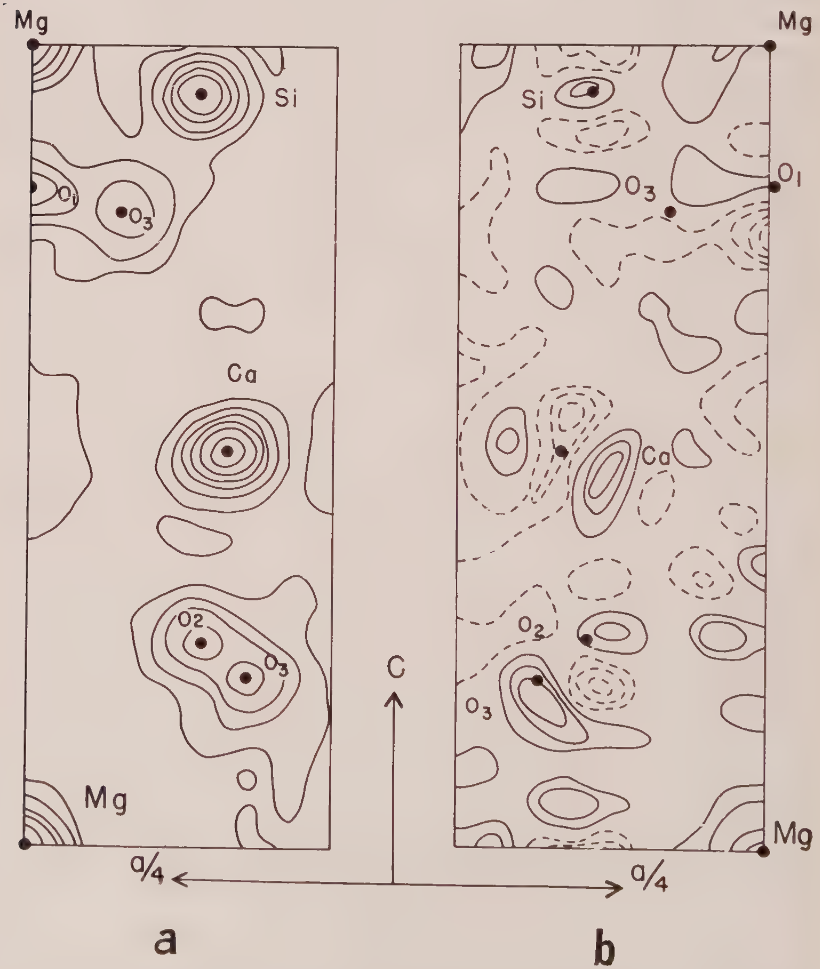

FIG. 1 (*a*) *y*-axis projection of the F_0-synthesis. Contours at arbitrary units of 50 around O atoms and 100 around other atoms. (*b*) *y*-axis projection of the $F_0 - F_c$ synthesis. Contours at units of 10 on the same scale as that of (*a*).

of position for the origin of the unit cell, the y-axis projection becomes centrosymmetric. The empirical atomic-scattering curves given by Bragg and West (1929) were used in the calculations. Weighted means of these atomic-scattering curves were used in order to take account of the atomic substitution in the melilite. As shown earlier in the paper, there was some doubt as to the composition of the melilite. There was, therefore, some doubt as to the scattering factors. Whether or not Fe″ is present makes little difference to the scattering factors for the "Ca" and "Si" atoms. The scattering factor for the "Mg" atom, however, varies greatly with the percentage of "Fe" in the structure as shown in columns *a* and *b* of Table 5. For convenience, the "Si" scattering factor was also used for the "Mg" atom in the preliminary calculations.

There was fair agreement between the observed and calculated structure amplitudes. An F_0-synthesis was computed (Fig. 1*a*) and more accurate atomic coordinates were obtained. The structure amplitudes were recalculated for the new coordinates and they then agreed slightly better with the observed structure amplitudes. After changing the "Mg" scattering factor, good agreement was obtained. The observed structure amplitudes were placed on an absolute scale by comparison of the observed and calculated structure amplitudes in the following way. The ratio of the mean values of the observed and calculated structure amplitudes for seven ranges of $\sin\theta$ was plotted against $\sin\theta$ on a graph. The best curve was drawn between the points to reduce the statistical fluctuations, and values from the graph were used to put the observed structure amplitudes on an absolute scale and also to correct for the factors varying with $\sin\theta$. An (F_0-F_c) synthesis was computed in order to refine further the atomic coordinates (Cochran, 1951). As the three strongest structure amplitudes were definitely affected by extinction (see Table 3), they were not included in the (F_0-F_c) synthesis.

The resulting atomic positions did not lie on appreciable gradients of electron density, thus showing that the atomic coordinates were correct. However, exactly on the positions occupied by the "Ca," "Si," and "Mg" atoms, there were small but significant peaks. These showed that the atomic scattering factors had been wrongly estimated. The necessary alterations in the atomic scattering factors were calculated and the structure amplitudes were recalculated using the new scattering factors. A further (F_0-F_c) synthesis was calculated and is shown in Fig. 1*b*. It contained only small peaks which did not indicate any appreciable change in the atomic coordinates or in the atomic scattering factors. The refinement, therefore, was judged to be complete. The fluctuation of electron density over regions not close to the atoms is about $2e/A^2$. There is a small peak on the silicon atom of $2e/A^2$ indicating a possible

TABLE 3. CALCULATED AND OBSERVED STRUCTURE AMPLITUDES

h	l	F_0	F_c
0	0	—	
	1	26.0	18.0
	2	32.0	27.6
	3	37.2	$\overline{38}.4$
	4	54.8*	69.2
	5	8.4	$\overline{6}.4$
	6	19.6	14.0
	7	30.0	$\overline{30}.0$
	8	7.6	11.2
	9	25.6	$\overline{18}.0$
	10	7.2	9.6
	11	10.1	$\overline{9}.6$
2	0	12.0	$\overline{16}.0$
	1	41.2	42.8
	2	11.2	$\overline{11}.2$
	3	27.6	24.8
	4	7.2	$\overline{6}.8$
	5	27.2	26.8
	6	3.2	2.8
	7	20.0	18.4
	8	x	.8
	9	10.0	12.0
	10	x	.4
	11	11.6	9.2
4	0	43.6*	$\overline{60}.4$
	1	14.8	11.6
	2	12.4	$\overline{14}.0$
	3	20.0	17.6
	4	15.2	$\overline{16}.8$
	5	29.2	28.8
	6	14.0	10.8
	7	27.6	28.0
	8	5.6	6.0
	9	27.2	19.2
	10	7.2	6.0
	11	14.8	11.6
6	0	55.2*	74.4
	1	x	$\overline{6}.8$
	2	42.8	45.6
	3	12.8	$\overline{12}.8$
	4	36.0	38.0
	5	14.0	$\overline{16}.0$
	6	20.4	20.8
	7	15.2	$\overline{15}.2$
	8	11.2	14.0
	9	17.6	$\overline{12}.8$
	10	7.6	10.0
1	1	14.8	14.0
	2	31.2	34.0
	3	17.2	17.6
	4	11.2	10.4
	5	3.6	9.2
	6	19.6	17.2
	7	8.0	5.6
	8	3.4	3.6
	9	9.2	$\overline{6}.0$
	10	x	0.0
	11	5.6	$\overline{5}.2$
3	1	33.6	39.6
	2	10.8	$\overline{12}.4$
	3	34.4	$\overline{38}.4$
	4	37.2	$\overline{37}.6$
	5	7.6	$\overline{6}.4$
	6	16.4	$\overline{14}.8$
	7	x	$\overline{0}.8$
	8	8.8	$\overline{8}.4$
	9	8.0	7.2
	10	x	$\overline{2}.4$
	11	10.4	9.8
5	1	15.6	$\overline{18}.0$
	2	11.6	$\overline{9}.2$
	3	2.0	$\overline{1}.2$
	4	2.8	1.6
	5	10.4	$\overline{11}.2$
	6	9.2	$\overline{6}.4$
	7	5.6	$\overline{4}.8$
	8	6.4	5.2
	9	x	.8
	10	x	2.0
7	1	x	$\overline{2}.0$
	2	19.6	18.2
	3	22.8	26.0
	4	22.4	22.4
	5	6.4	10.0
	6	16.4	15.2
	7	8.0	6.8
	8	5.6	6.0
	9	9.6	$\overline{5}.6$
	10	x	$\overline{1}.2$
8	0	9.2	12.4
	1	31.6	34.4
	2	16.4	12.8
	3	27.2	25.2
	4	x	00.0
	5	5.6	8 8
	6	5.6	$\overline{5}.6$
	7	8.8	8.0
	8	6.0	$\overline{5}.6$
	9	x	2.0
	10	7.6	$\overline{4}.8$
10	0	16.8	$\overline{16}.4$
	1	9.2	11.6
	2	15.2	$\overline{14}.0$
	3	9.2	10.0
	4	4.4	$\overline{5}.6$
	5	21.6	22.0
	6	6.8	4.0
	7	15.2	17.6
	8	x	2.0
	9	18.8	16.0
	10	x	2.8
12	0	21.2	23.2
	1	11.2	$\overline{14}.4$
	2	14.0	16.4
	3	11.2	$\overline{14}.4$
	4	17.2	21.6
	5	x	$\overline{4}.4$
	6	20.8	20.0
	7	x	$\overline{4}.8$
	8	13.2	15.6
14	0	14.8	12.0
	1	16.4	19.2
	2	10.0	6.0
	3	13.2	13.2
	4	x	2.4
	5	x	6.4
16	0	x	$\overline{1}.6$
	1	12.0	13.6
	2	x	$\overline{2}.4$
	3	7.6	11.2
9	1	4.8	7.6
	2	x	0.4
	3	x	$\overline{0}.4$
	4	8.4	$\overline{7}.2$
	5	x	4.4
	6	x	$\overline{3}.6$
	7	6.0	5.2
	8	x	$\overline{4}.8$
	9	x	4.0
	10	x	$\overline{4}.4$
11	1	x	$\overline{1}.6$
	2	10.4	$\overline{7}.6$
	3	13.2	$\overline{14}.0$
	4	10.0	$\overline{9}.2$
	5	8.4	$\overline{9}.2$
	6	10.0	$\overline{6}.4$
	7	5.6	$\overline{5}.6$
	8	x	0.8
13	1	x	3.6
	2	6.4	6.0
	3	x	1.2
	4	x	2.4
	5	x	0.4
	6	8.8	7.2
15	1	x	2.4
	2	5.2	3.6
	3	6.8	6.8
	4	x	3.6

* Affected considerably by extinction.
x Too weak to be recorded.

small increase in the atomic scattering factor. There is a negative peak flanked by two positive peaks at the Ca atom, indicating anisotropic temperature vibration with the largest vibration approximately parallel to the (001) plane. There are small peaks near to the positions occupied by the oxygen atoms. All the peaks near to the atomic positions are of approximately the same height as peaks far from the atoms and therefore are of doubtful significance. No adjustments have been made for these possible changes.

TABLE 4. ATOMIC COORDINATES AS FRACTIONS OF THE LATTICE PARAMETERS

Atom	x	y	z
Ca	0.3355	(0.5−x)	0.5073
Si	0.1396	(0.5−x)	0.9412
Mg	0.0000	0.0000	0.0000
O_1	0.5000	(0.5−x)	0.1804
O_2	0.1450	(0.5−x)	0.2583
O_3	0.0820	0.1820	0.7909

TABLE 5. ATOMIC SCATTERING CURVES USED IN THE STRUCTURE-FACTOR CALCULATIONS

Sin θ/λ	Ca	Si	Mg	O	a	b
0.0	19.0?	13.3?	10.7?	10.0?	10.7?	17.0?
0.1	16.2	11.6	9.4	8.0	9.4	13.8
0.2	13.1	9.8	7.8	5.8	7.8	11.3
0.3	10.5	8.3	6.5	3.7	6.5	9.3
0.4	8.5	6.8	5.2	2.5	5.2	7.6
0.5	7.2	5.6	4.1	1.7	4.1	6.2
0.6	6.0	4.6	3.2	1.1	3.2	5.1
0.7	5.1	3.6	2.5	0.7	2.5	4.2
0.8	4.3	3.0	1.9	0.5	1.9	3.5
0.9	3.7	2.5	1.5	0.4	1.5	2.9
1.0	3.1	2.0	1.2	0.3	1.2	2.5
1.1	2.6	1.6	1.0	0.2	1.0	2.1
1.2	2.3	1.4	0.9	0.1	0.9	1.8

The final reliability factor $\Sigma|F_0-F_c|/|F_0|$ is 0.13, neglecting the three planes affected considerably by extinction. The observed and calculated structure amplitudes are given in Table 3, the atomic coordinates in Table 4, the atomic scattering factors in the first four columns of Table 5. The random errors in the atomic coordinates were estimated by the method of Cruickshank (1949) using the following modifications. The profiles of the atomic peaks were taken from the F_0-synthesis and the errors in the observed electron density were found directly from the final (F_0-F_c) synthesis, at regions between the atoms. The random errors in the atomic coordinates are given in Table 6 and the calculated interatomic distances together with their standard errors are given in Table 7.

TABLE 6. RANDOM PROBABLE ERRORS OF THE ATOMIC COORDINATES

Atom	Error
Ca	0.003_3 Å
Si	0.004_4 Å
O	0.015_0 Å

TABLE 7. INTERATOMIC DISTANCES AND THEIR PROBABLE ERRORS

Atom	Distance (Å)	Error (Å)
$Si—O_1$	1.65_4	0.00_8
$Si—O_3$	1.64_3	0.01_6
$Si—O_2$	1.59_2	0.01_6
$O_3—O_3'$	2.60_0	0.02_1
$O_3—O_2$	2.74_9	0.01_9
$O_3—O_1$	2.56_2	0.01_5
$O_2—O_1$	2.72_0	0.01_8
$Mg—O_3$	1.87_6	0.01_5
$Ca—O_3$	2.43_8	0.01_5
$Ca—O_3'$	2.71_2	0.01_5
$Ca—O_2$	2.44_2	0.01_5
$Ca—O_2'$	2.68_7	0.01_5
$Ca—O_1$	2.44_4	0.01_1

The analysis deduced from the observed structure amplitudes and the chemical analyses give:

$$(Ca_{1.7}Na_{0.2}K_{0.1})\ (Mg_{0.5}Al_{0.4})\ (Si_{2.0}Al_{small})O_7 \text{ (to nearest 0.1)}$$

with variations possible for the substitutions Na↔Ca, Mg↔Al↔Si as these substitutions have little effect on the structure amplitudes. There can be little if any Fe in the structure, for the presence of the heavily scattering Fe atoms would considerably affect the structure amplitudes. The mean atomic scattering factors for the "Mg" atom with Fe present and with Fe absent are given in columns *a* and *b* of Table 5. The observed scattering factor is given under Mg in Table 5 and was found to be so close to column *a* that identical figures are given. The presence of one-tenth of the Fe given in the analyses 1, 3, 4, and 5 of Table 2 would give a significant peak on the (F_0-F_c) synthesis. Analysis 2 contains less iron but even this is too much. The deficiency of (Mg+Al) in the second group is a little disturbing. Better agreement with the *x*-ray data would be obtained if extra Mg were to replace Al but this would make the composition differ even more from the chemical analyses.

As with other mineral series, the refractive indices of melilite are a function of composition. Data on the pure Ak—Ge series (synthetic) are given by J. R. Goldsmith (1948*a*). At 55 per cent Ak the crystals are uniaxial with $\omega=\epsilon=1.65$. The effect of replacement of Ca by Na is not given for the Ak—Ge series except for the end-member, Ge. For this member, the effect is to reduce ω and ϵ and to make the crystal optically more negative. Assuming that the replacement by Na has the same effect throughout the series, then for the composition deduced from the structure factors and the chemical analyses of Capo di Bove melilite, the refractive indices should be reduced from 1.65 and the crystal should become negative. The values of $\omega=1.638$, $\epsilon=1.634$, found by MacKenzie are in rough agreement with the *x*-ray value in indicating a composition near 60 per cent Ak and some replacement by Na. Comparison of the values of *a* and *c* with those obtained by Andrews (1948) and Ervin and Osborn (1949) gives akermanite percentages of 75 and 85 (Andrews) and 65 and 100 (Ervin and Osborn). The presence of Na and other substituents complicates these deductions also.

All indications, however, show that this melilite is nearer to the Ak end of the melilite series with about 60 per cent Ak and some substitution by Na.

Discussion of the Structure

This work has confirmed the structure obtained by Warren and testifies to the accuracy of his determination. The use of modern, more accurate, techniques has produced more accurate coordinates than those of Warren, but this was to be expected. The structure obtained by Raaz (1930) for synthetic gehlenite has the same atomic positions as those in melilite.

The *z*-axis projection of the melilite structure is shown in Fig. 2. The melilite structure consists essentially of twisted sheets of tetrahedra linked parallel to (001). The sheets are held together by calcium-oxygen linkages. As the tetrahedral binding in the sheets should be stronger than the calcium-oxygen binding between the sheets, the strongest cleavage should be parallel to (001). The weakest binding in the sheets probably is across the (110) planes, as these planes leave intact most of the tetrahedral bonds. In accord with these deductions a moderate cleavage parallel to (001) and a poor cleavage parallel to (110) are recorded for the various melilites.

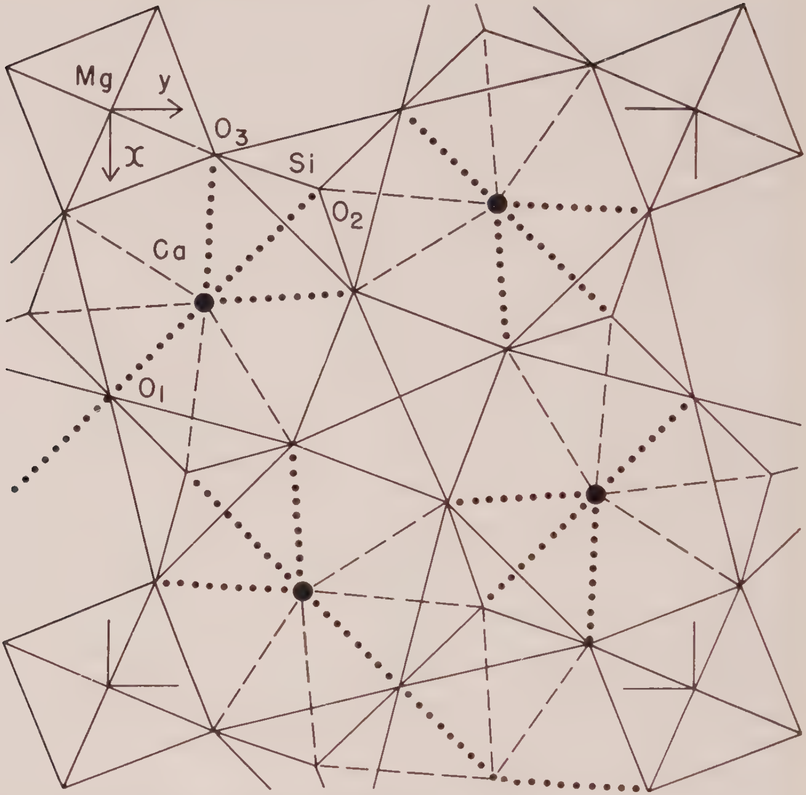

FIG. 2. z-axis projection of the melilite structure. The tetrahedra are outlined by unbroken lines. The broken lines show long Ca—O distances and the heavy dotted lines show short Ca—O distances.

There is little doubt that all the melilites have the same structure apart from the atomic substitution. The arrangement of Mg, Al, and Si atoms in the tetrahedra is of interest for they may be distributed in various ways inside the tetrahedra. It is unlikely that Mg and Si share the same tetrahedron because of the difference in ionic radii. Substitution between Al and Si is well known in the feldspars, and substitution between Al and Mg is possible because the ionic radii are not greatly different. For åkermanite, $Ca_2MgSi_2O_7$, the Mg atom would be expected to occupy the tetrahedron at the origin of the unit cell (for convenience, this will be called tetrahedron 1) and the 2 Si atoms would be expected to occupy the other two tetrahedra which are equivalent (for convenience, these tetrahedra will be called 2 and 3). In gehlenite, $Ca_2Al_2SiO_7$, substitution between Al and Si is possible in all the tetrahedra. The two extreme cases of ordering are: (*a*) 1 Al in tetrahedron 1 and (1 Al and 1 Si) in tetrahedrons 2 and 3; (*b*) 1 Si in tetrahedron 1 and 2 Al in tetrahedrons 2 and 3. For case (*a*), there would be only statistical satisfaction of the space group symmetry but this does not rule out the possibility. Intermediate stages of ordering are possible.

If only the two extreme cases of ordering are considered, the possible arrangement of atoms through the whole Ak—Ge series is shown in Fig. 3. If no substitution between Mg and Si can occur, the distribution is as shown by the full lines with Al linearly replacing Mg, while the corresponding change of Al for Si occurs in the other tetrahedron. However, it would be expected that the other gehlenite structure would be more stable as each tetrahedron then contains only one type of atom. If this structure is really the more stable one, there is probably a change in the mode of substitution somewhere in the series as indicated by the dotted lines. It is possible that the ordering of the atoms in melilite changes with time, and therefore the synthetic melilites may differ from the natural melilites.

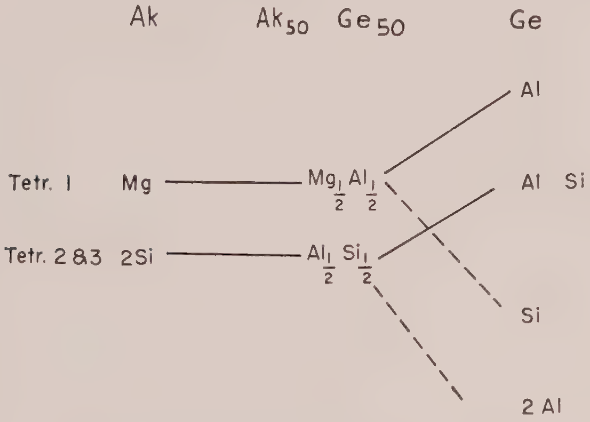
Ak
Ak_{50} Ge_{50}
Ge
Al
Tetr. 1
Mg
$Mg_{\frac{1}{2}} Al_{\frac{1}{2}}$
Al Si
Tetr. 2 & 3
2Si
$Al_{\frac{1}{2}} Si_{\frac{1}{2}}$
Si
2 Al

FIG. 3. Possible substitution in the Ak—Ge series.

The lattice parameter measurements on the synthetic Ak—Ge series by Andrews (1948) and Ervin and Osborn (1949) show a continuous change with composition. Measurements of the refractive indices of the synthetic Ak—Ge series by Goldsmith (1948*a*) also show a continuous change with composition. The first ordering reaction gives a completely smooth substitution of the atoms and would explain the continuous curves. For the second ordering reaction, the substitution of the atoms may or may not be a continuous function of composition according to the exact nature of the substitution. If only Al replaces the Mg at the akermanite end of the series and then there is a sharp change with the Si moving into tetrahedron 1, there should be a discontinuity in the lattice parameters. However, if there is a gradual change in the substitution of Si for (Mg, Al) there will be no discontinuity but there may be a change of slope in the graph of the lattice parameter, or refractive index, against composition. As there is no discontinuity either in the lattice parameters or refractive indices and no appreciable discontinuity in the first derivative, it is not possible to decide between the two forms of ordering.

It should be possible to determine the ordering of the Mg, Al and Si atoms by accurate determinations of the sizes of the tetrahedra by means of single crystal *x*-ray methods. The expected Si—O, Al—O, and Mg—O distances are respectively about 1.6 Å, 1.75 Å, and 1.9 Å. The mean cation-oxygen distances found in this work are $1.87_6 \pm 0.01_5$ Å for tetrahedron 1, and $1.63_3 \pm 0.01_1$ Å in tetrahedra 2 and 3. The melilite from Capo di Bove, therefore, shows a definite separation of the Si from the Mg and Al, as would be expected. The Capo di Bove melilite is not represented on the Ak—Ge series because of the substitution of Na and K. If only the Mg:Al ratio is considered, the nearest point on the Ak—Ge series is at about 60 per cent Ak, 40 per cent Ge. It is extremely likely that all the other natural melilites at the Ak end of the Ak—Ge series have the same segregation of the silicon atoms.

The only other melilite, the coordinates of which have been worked out, is synthetic gehlenite (Raaz, 1930). Raaz could not determine the ordering of the atoms because the technique for measuring interatomic distances was not sufficiently accurate. He considers that the arrangement of 1 Si in tetrahedron 1 and 2 Al in tetrahedra 2 and 3 is more likely, from space group considerations, and gives that as his determined structure.

Further accurate single crystal work is necessary to determine the ordering in the melilites. Accurate determination of both the natural and synthetic gehlenite would fix the ordering in this end-member of the series.

The melilites have commonly been regarded as belonging to the pyrosilicates with a Si/O ratio of 2/7. The Si:O ratio is not always a good criterion for the classification of silicate structures. A better criterion, sometimes, is one expressing the linking of the tetrahedra in the structure. This may be obtained by taking the *X*:*O* ratio where *X* represents all the cations in the centers of the oxygen tetrahedra. For the melilites, *X* is Si, Al and Mg (with possible other substitutions). This ratio is 3:7 for the melilites and lies between the values of 1:2 for the feldspars and 2:5 for the micas. The *X*:*O* ratio remains constant throughout the Ak—Ge series, whereas the Si:O ratio varies from 2:7 at Ak to 1:7 in Ge. The Si_2O_7 group in the Ak structure and the possible Al_2O_7 group in the Ge structure are best regarded as ordering of the cations in a more complex linking of tetrahedra.

From the geometrical point of view, the following substitutions are possible:

(1) Ca, Na, K
(2) Mg, Al, Fe″, Fe‴, Mn, Ti, Zn
(3) Si, Al

Berman (1929) has calculated the analyses of 23 melilites. He assumes that there are 70 oxygen atoms in the structure and adds up the (Ca, etc.) in one group and the (Mg, etc., Si, etc.) in another group. If the ideal formula of the melilites holds true then these two groups add up to 20 and 30 respectively. Figure 4 is a histogram of the results. For group 1, the mean is 19.5 and apart from one result at 17.2 the analyses are con-

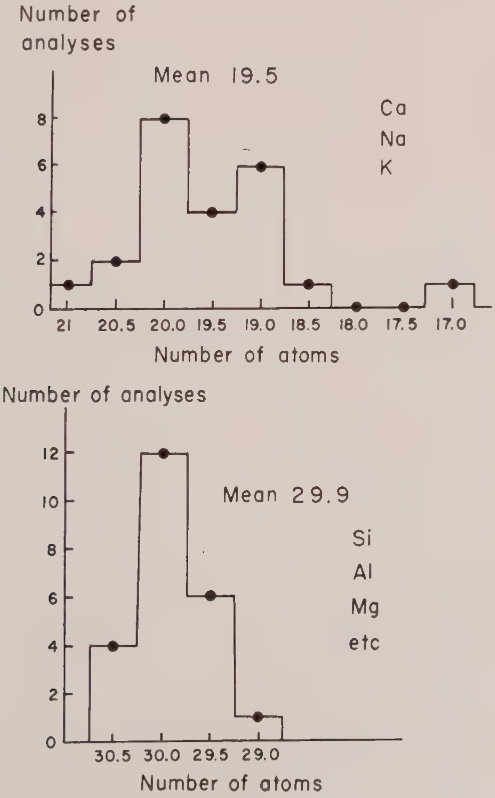

FIG. 4. Histograms of the analyses used by Berman.

fined to a spread of about 1. The 17.0 result must be regarded with some suspicion. In group 2, the mean is 29.9 and the spread of the results is confined to 1. There is little doubt from these results, as Berman stated, that melilite has the formula $(\text{Ca, etc.})_2\,(\text{Mg, etc.; Si, etc.})_3\text{O}_7$. In only one analysis is the silicon greater than 20 (viz., 20.7). This confirms the segregation of the silicon from the other elements deduced from the geometrical considerations of the crystal structure.

Berman (1929) points out that the sum of (Ca, etc.) is lower than the ideal value of 20.0. Goldsmith (1948) points out that the sum of (Mg, etc.)

TABLE 8. SOME MELILITE ANALYSES

	1 Melilite Sugar loaf series, Honolulu		2 Melilite Mt. Elgon, Uganda		3 Gehlenite Fassathal, Tyrol		4 Gehlenite Luna County, New Mexico		5 Melilite Iron Hill, Colorado		Mean
	Wt.%	Atoms	Wt.%	Atoms	Wt.%	Atoms	Wt.%	Atoms	Wt.%	Atoms	
SiO_2	42.81	19.42	42.86	19.58	30.09	13.59	32.60	14.80	43.27	19.66	
Al_2O_3	6.59	3.52	5.02	2.70	21.67	11.53	18.10	9.69	6.44	3.45	
Fe_2O_3	1.90	0.65	0.26	0.09	1.36	0.46	0.95	0.32	0.97	0.33	
FeO	3.06	1.16	2.99	1.14	2.14	0.81	0.92	0.35	2.32	0.88	
MnO	0.08	0.03	0.08	0.03	0.04	0.01	0.02	0.01	0.16	0.06	
MgO	7.48	5.05	9.20	6.26	3.87	2.60	6.91	4.67	7.90	5.35	
CaO	33.27	16.16	34.90	17.08	38.36	18.55	40.08	19.49	34.76	16.92	
Na_2O	3.75	3.30	3.68	3.26	0.75	0.66	0.18	0.16	3.59	3.16	
K_2O	0.33	0.19	0.42	0.25	0.16	0.09	0.21	0.12	0.20	0.11	
TiO_2	0.12	0.05	0.06	0.02	tr		0.00		tr		
ZnO	n.d.		n.d.		n.d.		n.d.		n.d.		
P_2O_5	n.d.		n.d.		0.00		0.00		0.00		
H_2O^+	0.43	1.30	0.22	0.67	1.64	4.94	0.48	1.46	0.28	0.85	
H_2O^-	0.00		0.00		0.00		0.00		0.00		
Sum	99.82		99.69		100.08		100.45		99.89		
Sum Ca, etc.		19.65		20.59		19.30		19.77		20.19	19.90
Sum Si, etc.		29.88		29.82		29.00		29.84		29.73	29.65
Sum Ca, etc. Sum Si, etc.	If neglect H_2O										20.16 30.04

Analyst: H. B. Wiik, Finland.

is very close to 30 (actually 29.9) and therefore the errors in the analyses should be small and the deficiency of (Ca, etc.) is real. If the poor result be neglected at 17.2, the deficiency of (Ca, etc.) is reduced a little from 0.5 atoms to 0.4 atoms, but it is still appreciable. In a series of heating experiments he attempted to explain the substitution of Na for Ca. He heated $Na_2Si_3O_7$ with Ak—Ge mixtures and found that for Ge, 3.85 per cent by weight of Na_2O entered the structure whereas no Na_2O entered the Ak.

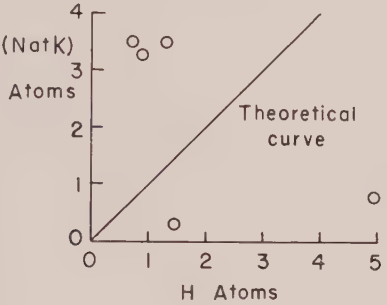

FIG. 5. Graph of (Na+K) and H atoms for some melilite analyses.

In effect he was making the substitution Ca→Na together with (Mg, Al)→Si. This amount of Na_2O was not sufficient to explain the Na_2O in the natural melilites. He suggested that the only reasonable way of replacing Ca by Na is by making the corresponding replacement O″ to OH′. Unfortunately, nearly all the analyses considered by Berman do not contain water, presumably because it was not determined, and no test could be made of this hypothesis. By courtesy of K. J. Neuvonen, some further analyses of natural melilites, made by H. B. Wiik of the Geological Survey of Finland, have been placed at my disposal. These are reproduced in Table 8. The melilites vary from the akermanite end to the gehlenite end. The analyses show considerable amounts of H_2O^+ water (i.e., water not removed by heating to 100° C.). The analyses were computed to 70 oxygen atoms (including water). The mean (Ca, etc.) is 19.90 atoms which is very close to 20. The mean (Si, etc.) is 29.65, which is rather low. These results differ from the analyses considered by Berman as they have a closer agreement for (Ca, etc.) and a poorer agreement for (Si, etc.). On Goldsmith's theory of the OH replacement there should be a relation between the proportions of Na and H atoms. Figure 5 is a graph of this. If the presence of Na is caused solely by the presence of H_2O then the graph points should fall on the straight line. This is definitely not true. However, it is still possible that some of the Na is explained by the H_2O and the rest explained by other mechanisms.

However, analysis 3 has 4.94 H atoms and only 0.75 atoms of (Na+K); analysis 4 has 1.46 H atoms and only 0.28 atoms of (Na+K). There is no doubt, therefore, that Goldsmith's hypothesis does not explain these melilite analyses and another explanation of the role of H_2O is needed. It is still possible that it does occur in the structure as OH' groups, in which case, the most probable position of the OH groups is at the only unshared corner of the tetrahedra, O_2. Megaw (1949) has shown that in afwillite OH groups form some of the corners of the silicon tetrahedra, but it is the only known structure in which this has been found with certainty. The unshared corner of the melilite tetrahedron has insufficient valence bonds for an O'' ion on the basis of Pauling's rule of electrostatic valence bonds (see later). It is not very unlikely, therefore, that an OH group could go into the structure at this point. However, if the chemical analyses are recalculated with the water neglected, slightly better agreement for the sum of (Ca, etc.) and (Mg, Si, etc.) is obtained. The old totals are 19.90 and 29.65, and the new ones, 20.16 and 30.04. The significance of the water in the melilite analyses must be regarded as uncertain; apart from the role of H_2O, the melilite analyses are well explained on a geometrical basis of atomic substitution. Goldsmith's failure to produce a synthetic melilite containing sufficient Na_2O is not explained.

The detailed shapes of the polyhedra in this melilite structure are of interest. As mentioned earlier, the segregation of the (Mg, Al) from the Si was deduced from the sizes of the tetrahedra. There are only two independent O—O distances in the MgO_4 tetrahedra; these have similar lengths of 3.11 and 3.04 Å, showing that the tetrahedron is almost regular in shape.

The two Si tetrahedra are related by a plane of symmetry and each tetrahedron also has a plane of symmetry passing through it. The distances in the Si tetrahedra are: Si—O_1, $1.65_4 \pm 0.00_8$; Si—O_2, $1.59_2 \pm 0.01_6$; Si—O_3, $1.64_3 \pm 0.01_6$ (twice); O_3—O_2, $2.74_9 \pm 0.01_9$ (twice); O_1—O_2, $2.72_0 \pm 0.01_8$; O_3—O_3, $2.60_0 \pm 0.02_1$; O_1—O_3, $2.56_2 \pm 0.01_5$ Å (twice). The mean Si—O distance of $1.63_4 \pm 0.01$ Å compares well with the sum of the theoretical ionic radii 1.60 Å for Si—O and the values 1.60 ± 0.01 for Si—O in afwillite (Megaw, 1952), 1.61 ± 0.02 for Si—O in tilleyite (Smith, 1952*a*), 1.642 for $Si_{3/4}Al_{1/4}$—O in sanidinized orthoclase (Cole, Sorum, and Kennard, 1949); and $1.69_6 \pm 0.02$ Å for $Si_{1/2}Al_{1/2}$—O in paracelsian (Smith, 1952*b*) when account is taken of the possible substitution of the Si by the larger Al ion in melilite. Pauling (1929) discusses the deformation of coordination polyhedra, and states: (*a*) shared edges are shortened while unshared edges are correspondingly lengthened, and (*b*) electrostatic repulsion increases the separation of neighbouring cations. A detailed study of the cation-cation forces does not explain the variation of

Si—O distances. A possible explanation of this variation is given later. The variation of the O—O distances is explained by the sharing of edges; for the three short distances of 2.60 and 2.56 (twice) Å are for shared edges, and the three long distances of 2.75 (twice) and 2.72 Å are for unshared edges. In tilleyite, $Ca_5 \cdot Si_2O_7 \cdot 2CO_3$ (Smith, 1952*a*) the variations of Si—O and O—O distances in the structure were explained by Pauling's statements.

The coordination polyhedron of the Ca ion is distorted. The Ca ion has eight neighbors at distances of $2.43_8 \pm 0.01_5$ (twice); $2.44_2 \pm 0.01_5$; $2.44_4 \pm 0.01_5$; $2.71_2 \pm 0.01_5$ (twice); and $2.68_7 \pm 0.01_5$ Å (twice). This striking segregation into two groups of distances suggests that the Ca—O bonds are of two kinds. The shorter distances should correspond to stronger ionic bonds than the longer distances. Assuming that only the shorter distances correspond to bonds, the application of Pauling's rule of electrostatic valence bonds gives the following counts: O_1, 2.9; O_2, 1.4_5; O_3, 2.0_5 (assuming a composition of $Ca_{1.7}Na_{0.2}K_{0.1}Mg_{0.6}Al_{0.4}Si_{2.0}O_7$). There is a considerable deviation from the ideal value of 2.0 for O_1 and O_2. Assuming that all Ca—O bonds involve an equal transfer of electrons, we get the following valence counts: O_1, 2.4_5; O_2, 1.7_0; O_3, 2.0_5. The deviation is now only half as much. Only if the shorter bonds are completely neglected is it possible to get a valence balance: O_1, 2.0; O_2, 1.9; O_3, 2.0_5. It is probable that the Ca—O bonds are not truly ionic and have a considerable homopolar character. Pauling's rule would not then be expected to hold exactly. The deviation is, however, rather large. It is possible that the deviation is related to the variation in the Si—O distances as shown below.

Distance	1.59_2	1.64_3	1.65_4 Å
Valence bonds	1.4_5	2.0_5	2.9

The shorter the Si—O distance, the stronger should be the bond between the Si and O atoms and vice versa. This could balance the deficiency or excess in the sum of electrostatic valence bonds. The values given are in accord with this hypothesis.

It is well known that Ca polyhedra are irregular and numbers of oxygen neighbors from 6 to 9 have been recorded in different structures. Although the Ca—O distances in melilite are somewhat irregular, the polyhedron has a fairly regular shape, approximating the square Archimedean antiprism. Figure 6 is a representation of the Ca polyhedron on a stereographic projection. The O—Ca—O angles vary from 59° to 83°, the mean being 73°. The mean deviation of the O—Ca—O angles from the value of 73° is only 6°, showing that the steric coordination is undoubtedly a fairly regular square antiprism with 8-coordination. As men-

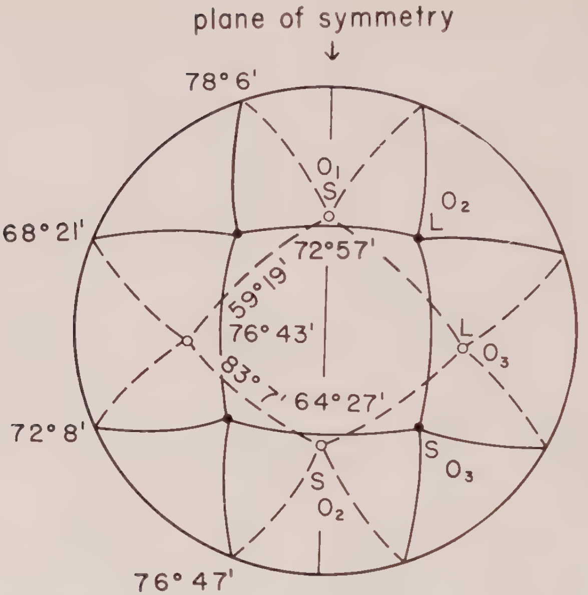

FIG. 6. The Ca polyhedron. S and L denote short and long Ca—O distances.

tioned earlier there is some doubt as to the exact electrostatic coordination because of the variation in the Ca—O distances and because of the deviation from Pauling's rule. Similar variations have been found in the recently determined structures of afwillite (Megaw, 1952) and tilleyite (Smith, 1952*a*). In these structures, there are 6 or 7 oxygen neighbors at varying angles and distances; it is also difficult to determine the electrostatic coordination. These variations are to be expected, for the main factor governing the packing of a silicate is the strong bond in the silicon tetrahedra. The steric hindrance between these strong tetrahedral groups usually prevents the formation of regular polyhedra around the Ca ions, for it is usually not possible to arrange the tetrahedra in such a way that the oxygen atoms lie at the corners of other regular polyhedra. The ideal coordination number of Ca is about 8, corresponding to a cube or a square antiprism. The observed variations from these ideal polyhedra are considerable and sometimes lead to difficulty in applying the geometrically based rules of Pauling. However, when the difficulties of packing together polyhedra of different sizes and shapes are considered, it is surprising that Pauling's rules explain so well the packing of crystal structures.

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DENSITY DETERMINATION BY A MODIFIED SUSPENSION METHOD; X-RAY MOLECULAR WEIGHT, AND SOUNDNESS OF SODIUM CHLORIDE

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Abstract

A modified suspension method for density determinations up to $d = 4.25$ g. cm.$^{-3}$ is described, according to which a pycnometer together with the heavy liquid and the substance (small crystal or fraction of it) is weighed after the pycnometer liquid has been adjusted to the mark at the suspension temperature. Knowing the volume of the pycnometer, the density of the liquid (= to that of the substance) is calculated. The accuracy of the method is at least 3×10^{-4} g. cm.$^{-3}$, and can be still further improved upon. About 3 hrs. are necessary to perform one determination.

The density of purest sublimed sodium chloride reduced to 20° C. was determined to 2.1638 ± 0.0003 g. cm.$^{-3}$. The *x*-ray molecular weight was then 58.430 ± 0.010, lower by 0.024 than the chemical weight. Therefore, NaCl contains vacant sites of at least 3.0×10^{18} per cm.^{3} at room temperature. One part of these vacancies may be assembled in the form of submicroscopic cracks or cavities in the inside of the crystals.

Introduction

For the precision determination of atomic and molecular weights by the *x*-ray-density method[1,2] reliable density data are necessary. The most precise results are obtained by the flotation or suspension method, which permits determinations of high precision up to $d = 4.25$ g. cm.$^{-3}$ By this method Bearden obtained one of the best density values for the diamond.[3] Johnston and Hutchison improved the density determinations[4] and obtained very precise values for lithium fluoride, sodium and potassium chlorides.[1]

However, the suspension method, as developed by the authors aforementioned, is difficult to apply, and it requires considerable time to perform one density determination. By some further modifications it was possible to simplify the operations, and to shorten the time required for a determination so that it could be performed in three hours. This method is described below. It was checked by the determination of the densities and the molecular weights of purest sodium chloride and silicon.

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[1] Hutchison, C. A., and Johnston, H. L. *J.A.C.S.*, **62,** 3165 (1940); **63,** 1580 (1941); Johnston, H. L., and Hutchison, D. A., *Phys. Rev.*, **62,** 32 (1942); Hutchison, C. A., *J. Chem. Phys.*, **10,** 489 (1942); Hutchison, D. A., *J. Chem. Phys.*, **13,** 383 (1945); Batuecas, T., *Nature*, **165,** 61 (1950).

[2] Straumanis, M., *Zeit. Physik*, **126,** 49 (1949).

[3] Bearden, J. A., *Phys. Rev.*, **54,** 698, 700 (1938).

[4] Johnston, H L., and Hutchison, C. A., *J. Chem. Phys.*, **8,** 869 (1940); Hutchison, D. A., *Phys. Rev.*, **66,** 144 (1944).

THE METHOD

The principle of the method is as follows: A piece of a substance, the density of which is to be determined, is immersed in a liquid having approximately the same density as has the substance; the substance, therefore, rises or sinks slowly in the test tube. To obtain the suspension of the substance in the liquid, both are transferred to a pycnometer of a special design, which then is immersed in the water of a thermostat, the temperature of which can be controlled accurately. By raising or lowering the temperature the suspension of the substance in the liquid can be easily achieved. At the suspension temperature the excess liquid is removed (down to the mark) from the pycnometer, and the latter is weighed together with the liquid and substance. Knowing the volume of the pycnometer at the suspension temperature, the density of the liquid, which is equal to the density of the substance at that temperature, can easily be computed. The application of this method is possible only if there is a difference in the cubical expansion coefficients of the liquid

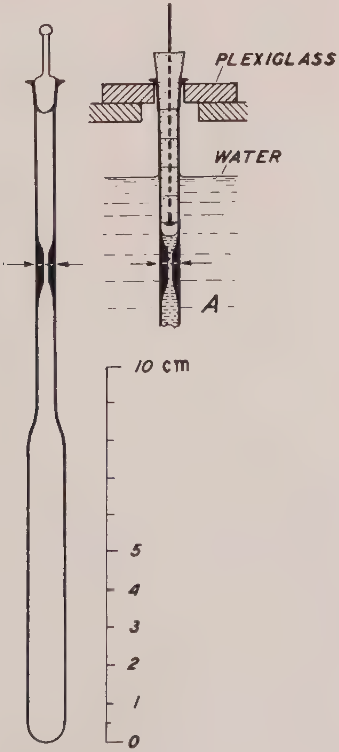

FIG. 1. Pycnometer for density determinations by the suspension method.

and of the substance, which is usually the case. The precision of the determinations increases with that difference. The section through the pycnometer is shown in Fig. 1.

The pycnometer of the dimensions as given in Fig. 1 was made of pyrex glass, heated in a furnace for 18 hrs at 600° C. in order to remove the internal stresses, and then slowly cooled. The pycnometer after being well cleaned was calibrated at 25, 30, 35 and 40° C., using triple distilled deaerated water. The volume did not change very much with temperature:

Temp. ° C.	25°.0	30°.0	35°.0	40°.0
Volume in cm.^{3}	4.76847	4.76870	4.76897	4.76930

The volume of the pycnometer for intermediate temperatures was obtained by interpolation. The temperature readings (accuracy ± 0.01°) were made with a thermometer which was compared with another one calibrated by the Bureau of Standards. The weights were also checked and all weighings were reduced to a vacuum. The weighing operations were always performed in the same manner; prior to each weighing the pycnometer stood for 10 minutes in the case of the balance. The funnel tube of the pycnometer was always filled during the experiment with a cork stopper, as shown in Fig. 1*A*, in order to prevent distillation of components of the heavy liquid to parts of the pycnometer which were at lower temperatures because they were outside of the water of the thermostat. The stopper was removed when, at a certain temperature, the suspension of the substance in the liquid has been attained. Immediately after this the excess water or heavy liquid was sucked by a capillary pipette and by needle-like filter paper strips from the funnel tube of the pycnometer down to the mark. Then the pycnometer, now closed with a glass stopper, was removed from the water bath, dried with chamois, and placed in the balance case where it was left for 10 minutes before being weighed.

The slow change of the water bath temperature and the temperature control was achieved by an adjustable contact thermometer connected through an electronic relay, and with an electric bulb immersed in the bath as a heater. A copper coil for cooling the water of the bath, if necessary, was also provided. The pycnometer was immersed in the water, as shown in Figs. 1*A* and 2, and the uniformity of the temperature distribution throughout the bath was assured by a stirrer. The adjusting of the level of the liquid, and the cleaning of the funnel tube of the pycnometer was done with the aid of a magnifying glass (Fig. 2). It was assumed that the density of the liquid was equal to that of the sample, if it did not change its position in the middle of the pycnometer during half an hour, as observed through the telescope of the cathetometer.

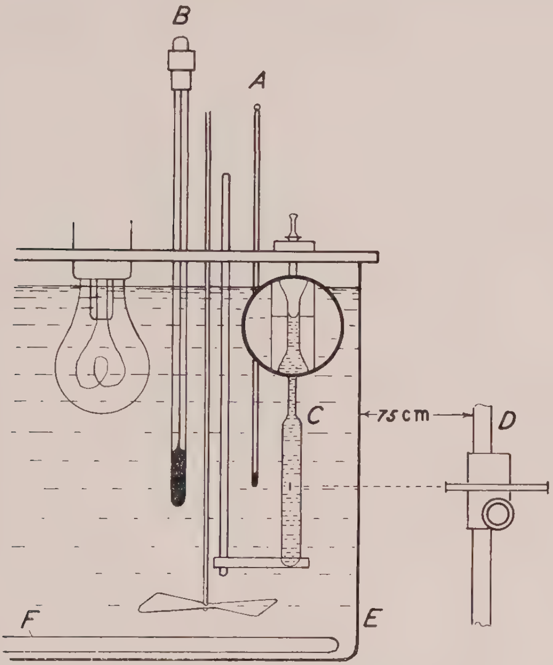

FIG. 2. Pycnometer with heavy liquid and sample in the water bath. *A*—thermometer. *B*—contact thermometer. *C*—pycnometer just before taking it from the bath. *D*—telescope. *E*—glass jar. *F*—cooling coil.

DENSITY OF PUREST SODIUM CHLORIDE AND OF SILICON

For the density determinations purest sodium chloride (Merck) was chosen. The reagent was sublimed in a quartz glass tube in a vacuum at 800° C. The small crystals which grew on the cooler parts of the tube were very clear and cubical in shape. The crystals were removed from the glass, and the best (being quite transparent, without cracks and signs of deformation) were chosen for the determinations. The size of these fragments was approximately 0.5×2 mm., so that they could freely pass the narrow neck of the pycnometer (Fig. 1). Just before the density measurements were made the crystals were heated for 10 minutes at 500° in air.

The heavy liquid used was bromoform.[5] It has a density of 2.87 g. cm.$^{-3}$, and ethyl alcohol was added in order to reach the density of sodium chloride. This can be done in a small test tube at room temperature, as previously mentioned. The liquid was saturated with sodium chloride. The sodium chloride crystals transferred together with the liquid to the pycnometer (Fig. 1) showed, of course, different suspension temperatures, because the composition of the liquid each time was not exactly the same. The densities of 9 crystals (out of 10 measured) at the suspension temperature are listed in Table 1. The densities were reduced to 20° C. using the equation:

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[5] Krumbein, W. C., Manual of Sedimentary Petrography, p. 320 (1938).

$$d_{t1} = d_{t2}[1 + \alpha(t_2 - t_1)]^3 \qquad t_2 > t_1,$$

d_{t1} is the density at 20° C., d_{t2} the density at the temperature measured, t_2 and t_1 are the respective temperatures, and α is the expansion coefficient of sodium chloride 40.5×10^{-6} at room temperature, as determined from *x*-ray measurements.[6] The table shows that the maximum deviation from the average density value is ± 0.0004 g. cm.$^{-3}$ The standard deviation[15] of the present measurements and the mean deviation is between ± 0.0002 and 0.0003. It is of no importance to mention the probable error as the measurements may still contain a systematic error which is greater than the probable error. The value obtained of $d_{20} = 2.1638$ for sodium chloride is larger than that obtained by Johnston and Hutchison[7]($d_{20} = 2.16360 \pm 0.00003$ g. cm.$^{-3}$).

TABLE 1. DENSITY AND *x*-RAY MOLECULAR WEIGHT OF PUREST, SUBLIMED SODIUM CHLORIDE

t in ° C.	d_t in g. cm.$^{-3}$	d_{20} in g. cm.$^{-3}$	M_x in g. mole^{-1}
26.12	2.16205	2.16365	58.427
24.82	227	355	23
26.90	186	368	27
24.10	234	342	20
25.24	270	408	38
27.20	213	403	36
24.89	262	390	33
26.50	194	365	26
25.57	273	420	41
	Average	2.1638	58.430
	Max. deviation	±0.0004	±0.010

The density of silicon was determined in the same way, using bromoform ethyl alcohol mixtures as a heavy liquid. About 20 determinations with 12 highest purity silicon crystals, containing only 0.03% carbon[8] were made. The accuracy of determination was approximately the same as in the previous case, at least $\pm 3\times 10^{-4}$ g. cm.$^{-3}$ For silicon an average value $d_{20} = 2.32831$ g. cm.$^{-3}$ was obtained.[9]

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[6] Straumanis, M., and Ievinš, A., *Zeit. anorgan. Chem.*, **238,** 175 (1938); see also Straumanis, M. E., and Aka, E. Z., *J.A.C.S.*, **73,** 5643 (1951).

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THE X-RAY MOLECULAR WEIGHT OF NACL AND SI.

The densities determined can be checked, computing the *x*-ray density (d_x) or atomic (A_x) or molecular weight (M_x), if the exact values of the lattice parameters of the substance under investigation are known. A convenient formula for this is as follows, if Siegbahn's wavelengths, expressed in X.U. or in kX are used[2]:

$$M_x = kN_s vd/n \qquad \text{g/mole} \tag{1}$$

where N_s is Siegbahn's Avogadro number (6.0594×10^{23}), v is the volume of the unit cell (in $kX^3 \times 10^{-24}$), d is the density (g. cm.$^{-3}$), and n the number of molecules per unit cell. k is a correction factor which eliminates the errors that were made determining N_s and the wavelengths. The necessity of such a factor for exact molecular weight calculations was previously emphasized by the author in 1944.[2] The correction factor k is the ratio:

$$\frac{M_1}{M_s} = k = \frac{100.095}{100.075} = 1.00020 \pm 0.00003 \tag{2}$$

where M_1 is the molecular weight of "purest" calcite, being a mixed crystal[10] of a composition similar to the one used by Siegbahn for his *x*-ray wavelength determinations. M_s is the molecular weight of calcite as accepted by Siegbahn for the calculation of the fundamental value for the lattice spacing of calcite.[11] Although the author's paper on atomic and molecular weight determinations, containing the most probable weight for calcite 100.095, was accepted by the Editor of *Zeit. f. Physik* in October 1944, the paper, because of the war did not appear until 1949.[2]

Birge (at the suggestion of Pabst), also came to the same conclusions concerning the molecular weight of calcite but he had the opportunity to publish his calculations in 1945.[12]

Of course, *x*-ray molecular weight calculations can also be made using Å units, but in this case the Avogadro number N_0 is necessary. This number can be determined easily from the relation[13,13a]:

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[9] Straumanis, M. E., and Aka, E. Z., *J. Appl. Phys.*, **23,** 330 (1952).

[10] Ievinš, A., and Straumanis, M., *Z. Physik*, **116,** 194 (1940); see also Andrews, K. W., *Mineral. Mag.*, **29,** 85 (1950). The analyses of the calcite crystals were made by M. Straumanis and A. Dravnieks: *Zeit. analyt. Chem.*, **120,** 168 (1940).

[11] Siegbahn, M., "Spektroskopie der Röntgenstrahlen," II Ed. Berlin, J. Springer (1931), p. 43.

[12] Birge, R. T., *Am. Journ. Phys.*, **13,** 67 (1945).

[13] Straumanis, M. E., *Acta Cryst.*, **2,** 83 (1949).

[13a] Straumanis, M., *Z. f. Physik*, **126,** 65 (1949).

$$N_0 = \frac{k}{(1.00202)^3} N_s = 6.02403 \times 10^{23} \text{ mole}^{-1} \text{ (chem. scale)} \qquad (3)$$

1.00202 being the conversion factor λ_g/λ_c, which is the ratio of wavelengths as determined from grating and from crystal measurements, k is the correction factor, eq. (2), previously established in 1944. Nevertheless N (in the physical scale) as calculated from N_0 (eq. 3) agrees closely with the recent value given by Du Mond and Cohen (in the physical scale)[14]:

$$N = (6.02544 \pm 0.00011) \times 10^{23} \text{ and from eq. 3 } (6.02567 \pm 0.00040) \times 10^{23} \text{ mole}^{-1}$$

The conversion factor from chemical to physical atomic weight units is 1.000272 ± 0.000005. In the first case the error given is the probable error, in the second case it is the standard deviation.[15]

Thus the equations for *x*-ray molecular weight (chemical scale) and density (d_x) calculations are as follows, if the wavelengths are expressed in Å units:

$$M_x = N_0 v^1 d/n, \quad \text{and} \quad d_x = nM/N_0 v^1 = nM/kvN_s. \qquad (4)$$

v^1 is the volume of the unit cell in $Å^3 \times 10^{-24}$ (v is in kX^3). Using N instead of N_0, the molecular weight in the physical scale is obtained.

All of the equations (1) and (4) are exact. Eq. (1) was used for the molecular weight calculations of sodium chloride and of silicon. The lattice parameter of purest sodium chloride for the calculation of v was taken from an earlier work[16]: $a_{25} = 5.62872 \pm 0.00003$ kX. The parameters for the respective temperatures at which the densities were determined were computed using the expansion coefficient of sodium chloride[6] at room temperature $\alpha = 40.5 \times 10^{-6}$. The data obtained are shown in Table 1. The output for the mean value of purest sodium chloride is 58.430 which is low by 0.024 or by 0.041% as compared with the chemical molecular weight 58.454. For silicon an average *x*-ray atomic weight of 28.083 was obtained,[9] which is higher than the old chemical value of 28.06, but is lower by only 0.007 than the new atomic weight[17] (28.09).

These discrepancies between the chemical and the *x*-ray molecular weights can be attributed to imperfections in the crystalline substances, or to experimental errors. In estimating these errors a choice can be made as to the two possibilities mentioned. However, some arbitrary factor f has to be introduced into the discussion that follows.

[14] Du Mond, J. W. M., and Cohen, E. R., *Amer. Scient.*, **40,** 447, 458 (1952).

[15] Wilks, S. S., Statistical Analysis, Princeton Univ. Press (1951), p. 36.

[16] Straumanis M., and Ievinš, A., *Z. f. Physik*, **109,** 728, 736 (1938).

[17] Wichers, E., *J.A.C.S.*, **74,** 2447 (1952).

SOUNDNESS OF SODIUM CHLORIDE CRYSTALS

The calculus method gives a good possibility for estimating the errors of more complicated measurements. The following equation was used for the calculation of the total error ΔM_x by which the *x*-ray molecular weight determinations (eq. 1) are affected:

$$\frac{\Delta M_x}{M} = \pm\left[\left(\frac{3\partial a}{a} f_1\right)^2 + \left(\frac{\partial k}{k} f_2\right)^2 + \left(\frac{\partial d}{d} f_3\right)^2\right]^{1/2} \qquad (5)$$

n and N_s of equation (1) are constants; ∂a, ∂k, ∂d are the standard deviations of the separate measurements, $\partial a/a \cdots$ are the relative errors, and f_1, f_2, f_3 are safety factors, each of them equal or larger than 1. The necessity of these factors follows from a consideration that relative errors are accidental or random errors; they reflect the quality of the measurements, but they do not contain the systematic error, which is undoubtedly in any measurement, and which may be even several times as large as the accidental error. It is the task of the investigator to estimate the value of the factor f for each kind of measurement, so that the systematic error becomes included in the deviation (e.g. $3\partial a f_1$).

It was assumed in the case of molecular weight determinations that

$$f_1 = f_2 = f_3 = 2,$$

would take care of the systematic errors. The equation as follows was obtained from eq. (5) for the total error (ΔM_x) of the molecular weight for both, silicon as well as sodium chloride:

$$\Delta M_x = \pm\ 2.8 \times 10^{-4} M. \qquad (6)$$

It was assumed that

$$\frac{\partial a}{a} = 5.3 \times 10^{-6};\ \frac{\partial k}{k} = 3 \times 10^{-5},\ \text{and}\ \frac{\partial d}{d} = 13.5 \times 10^{-5}.$$

The deviation ΔM_x may be called "standard absolute deviation."

The calculated error for the atomic weight of silicon according to eq. (6) is $\Delta M_x = \pm 0.008$. The *x*-ray-density weight is only 0.007 lower than the chemical value, and is, therefore, completely within the error limits calculated. Thus we can not come to a conclusion on the soundness of silicon crystals, and at present have to assume that the crystals do not contain any vacancies, or interstitial atoms.[13] The structure of silicon is sound within the errors of observation, but it is quite evident that eq. (1) can be used for checking the correctness of chemical atomic weights.

While the computed error (eq. 6) for sodium chloride is $\Delta M_x = \pm 0.016$, the difference in *x*-ray and chemical molecular weights is -0.024. As this difference considerably exceeds the above error of determination, we have to conclude that there are vacant sites in sodium chloride.[13]

The number of vacant sites per cm.^{3} can be easily computed, as the missing fraction of sodium chloride in the form of holes is about $0.024/58.5 = 4.1 \times 10^{-4}$ mole. Knowing the density, and Avogadro's number, 9.1×10^{18} vacant sites/cm.^{3} were found, assuming that each of these sites can be filled by only one ion. The error of the *x*-ray molecular weight determination is ± 0.016. If the weight were higher by this quantity, a minimum of 3.0×10^{18} vacancies/cm.^{3} at room temperature would be obtained. These concentrations of vacancies of approximately 1:2500 ions or of 1:7300 appear rather high, and it is important to check this result by other independent measurements.

This was possible because a theory of lattice defects has been developed by Schottky[18] and Wagner[19] in order to explain several qualities of crystals, e.g. the electrical conductivity of silver and alkali halides. Wagner and associates showed how to determine the number of vacant sites from conductivity measurements[19,20]. Seitz[21] estimated the number of defects in evaporated sodium chloride layers as being 10^{18} per cm.^{3}, and in metals such as copper in the vicinity of 10^{18} to 10^{19} per cm.^{3} at the melting point.[22] Further determinations were made by Etzel and Maurer,[23] finding the concentration of positive ion vacancies of a pure sodium chloride crystal as being 1.0×10^{17} per cm.^{3} at temperatures below 550° C. From measurements of dielectric constants Breckenridge computed that there are 2.1×10^{17} vacancies/cm.^{3} in sodium chloride at 85° C.[24]

Thus all these measurements and estimations show that the value of 9.1 or 3.0×10^{18} vacancies cm.$^{-3}$ determined for sodium chloride is very reasonable. Thereby the result obtained by the *x*-ray density method is a completely different, but a direct method.

The still existing difference may be explained by the fact that the conductivity methods detect only those vacancies which take part in the conductivity process. If, because of certain conditions, larger holes are formed, they contribute only partly to the total conductivity of the crystal. But the *x*-ray-density method detects all the holes, the small vacant sites as well as the submicroscopic cavities, and cracks, if they are inaccessible to the heavy liquid.

Manuscript received Sept. 8, 1952.

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FLUID INCLUSIONS IN MINERALS FROM ZONED PEGMATITES OF THE BLACK HILLS, SOUTH DAKOTA

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ABSTRACT

A study of fluid inclusions in minerals from zoned pegmatites was undertaken in an effort to check the hypothesis that zoned pegmatites formed through fractional crystallization in a restricted system. Beryl, spodumene, tourmaline, garnet and quartz containing fluid inclusions were heated, and temperatures of cavity filling were determined by the visual method.

Twelve pegmatites were sampled, but extensive results were obtained from only three pegmatites. Beryl from inner zones of the Bob Ingersoll No. 1 and Highland Lode pegmatites gave lower temperatures than beryl from outer zones. The Peerless pegmatite gave results that showed a reverse trend.

Temperatures observed in beryl ranged from 216 to 515° C. Results from individual crystals showed a range of 9 to 200° C., and individual zones showed ranges of 65 to 230° C.

Sources of error in interpretation are discussed, and an effort is made to calculate true temperatures of crystallization, insofar as available information permits.

Data were too meager to provide an adequate check on the hypothesis of fractional crystallization, although tentative support is given by results from two pegmatites. Estimates of pressures prevalent at the time of crystallization, together with inferred pressure-volume-temperature data, imply that some early-formed beryl crystallized at temperatures in excess of 500° C.

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INTRODUCTION

The existence of primary zonal structures in certain pegmatites has been recognized for many years. A paper by Cameron, Jahns, McNair and Page (1949) has offered the most recent evidence suggesting that zones develop through fractional crystallization of material in a restricted system. This paper gives the results of an attempt to check that hypothesis. If zoned pegmatites have crystallized from a restricted system, a systematic variation in temperature during crystallization may be expected. If this variation exists, it should be demonstrable by an examination of fluid inclusions. If the hypothesis is correct, fluid inclusions in minerals from outer zones might be expected to show disappearance of their vapor phases at higher temperatures than similar inclusions in minerals found in inner zones. It was hoped that a study of fluid inclusions would show whether such differences existed.

The pegmatites of the Black Hills, South Dakota, were selected as being best suited for the purposes outlined above. The pegmatites are well exposed, unaltered, and many consist of three to eight mineral assemblages in well defined zones (Page et al., 1952). More than 50 have been mapped in considerable detail. Fluid inclusions are known to exist in many of the pegmatite minerals. Beryl, which was found to be most satisfactory in earlier studies of this type (Cameron, Rowe and Weis, 1953) is known to occur in comparative abundance.

Twelve pegmatites, the New York, John Ross (Highland), Triangle A, High Climb, and Helen Beryl pegmatites in the Custer district, and the Bob Ingersoll No. 1 and No. 2, the Etta, Hugo, Peerless, Dan Patch No. 2, and Hesnard pegmatites in the Keystone district were sampled. Selection was based on the exposures available, number of zones, mineralogy, and detailed knowledge of their internal structure. Beryl, garnet, tourmaline, spodumene, amblygonite, apatite, microcline and quartz were collected. An effort was made to collect as many different minerals from as many different zones as possible. Euhedral crystals were collected wherever possible, to facilitate preparation of oriented sections.

After the specimens were sawed and polished, they were examined under the microscope. Those that were found to contain fluid inclusions were retained for further study in the heating stage. No fluid inclusions were found in microcline, apatite, or amblygonite. Beryl, spodumene (hiddenite), garnet, tourmaline and quartz were found to contain fluid inclusions in at least a few specimens.

More than 300 polished sections were prepared and examined; some 5,000 fluid inclusions were studied, and temperatures of disappearance were determined for approximately 1,100, including about 850 thought to be primary, and 250 of other types. Approximately 200 polished sections of beryl were made, including samples from all 12 pegmatites, but only 53 sections, from five pegmatites, were found to contain primary type inclusions in sufficient numbers to provide adequate temperature data. All temperature measurements on inclusions were made at least twice before they were considered valid. Those that could not be duplicated within 2° C. were discarded. It was found that temperatures obtained from a particular inclusion could ordinarily be duplicated many times, over periods of two to six months.

Description of Inclusions

It is essential in the use and interpretation of data from fluid inclusions that a distinction be made between primary and secondary inclusions. Unfortunately, some students of fluid inclusions in the past have made little or no effort to do this. No temperature data should be considered acceptable unless each inclusion studied is classified with respect to occurrence, behavior, distribution, shape, contents and relationship to crystallographic directions and secondary features of the host mineral. Proper interpretation can be made only after a thorough and careful examination of each and every polished section used. The indiscriminate use of data derived from fluid inclusions without proper attention to the recognition of criteria that may assist in distinguishing between primary, secondary, and doubtful inclusions must lead eventually to the accumulation of information that is largely meaningless.

Polished sections of Black Hills minerals were found to contain five types of inclusions, distinguishable by shape, distribution and contents. They may be divided into two groups: solid inclusions and fluid inclusions.

There are two kinds of solid inclusions present. One consists of euhedral to subhedral crystals of single minerals such as feldspars, tourmaline, quartz and mica (Fig. 1). The other consists of irregular shaped aggregates of fine-grained material, which appears to be made up of more than one mineral. Solid inclusions of both kinds were noted in beryl, quartz and tourmaline, but were not studied in detail.

The fluid inclusions can be divided into three general categories, distinguished on the basis of shape, distribution and relationship to crystallographic directions in the host mineral. Type I inclusions, consisting of a liquid and a gas, have shapes ranging from long, slender rods with rounded ends (Fig. 2) or irregular ends (Fig. 3) to shorter, broader shapes, showing negative crystal faces (Fig. 2). They all showed direct relationships to crystallographic elements in the host minerals. Elongate inclusions are invariably arranged with their long axes parallel to the *c*-axes of the beryl, spodumene, or tourmaline crystals in which they were found.

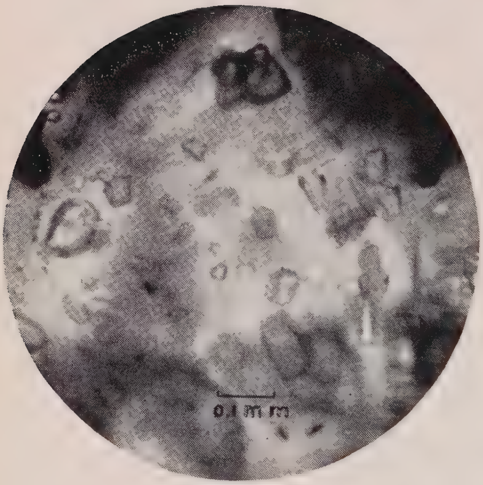


FIG. 1. Inclusions of individual mineral grains in tourmaline.

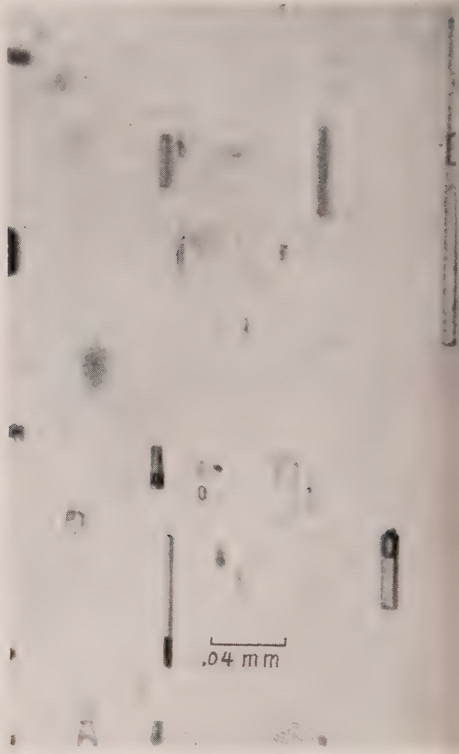


FIG. 2. Elongate fluid inclusions (Type I beryl. Uniform distribution and alignment par to crystallographic axes of the host mineral sug that the inclusions are primary.

Negative crystal cavities are arranged so that their faces are parallel to corresponding crystal faces in the host. Inclusions of this type are commonly found more or less evenly distributed throughout the crystals, or throughout considerable portions of the crystals, and are apparently unrelated to fractures or other secondary features. They are believed to have formed at the same time as the host minerals, and therefore are considered to be primary.

Type I. Elongate Type I inclusions with rounded ends were found in beryl and tourmaline. Spodumene characteristically contains cavities with irregular ends (Fig. 3). Beryl and garnet contain negative crystal cavities of various shapes. A few inclusions in spodumene contain in addition to the usual liquid and vapor phases, a solid, homogeneous material of unknown composition (Fig. 4). These inclusions give results in the same temperature range as those that had no included solids, and an

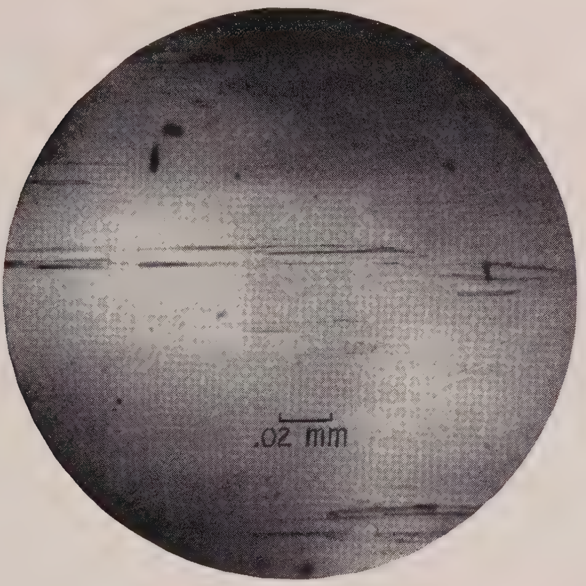


FIG. 3. Type I fluid inclusions in spodumene.

effort to dissolve the material by heating specimens to 600° C. was unsuccessful. The solid material is therefore interpreted as representing an accidental inclusion, rather than material that was precipitated out of solution from the liquid in the cavity.

Type II. Fluid inclusions of Type II were found in beryl, quartz and tourmaline. They consist of a liquid and a vapor phase, in irregular or rounded cavities that show no systematic relationship to either crystallographic elements or to recognizably secondary features. Some crystals contain hundreds of thousands of these inclusions, and nearly all speci-

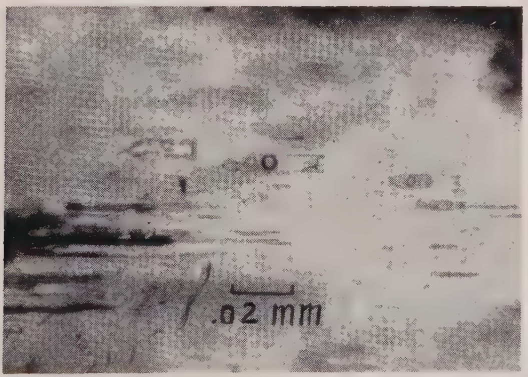


FIG. 4. Fluid inclusions containing mineral grains. Spodumene.

mens contained at least a few. They are almost invariably more numerous than Type I inclusions. They may be of primary origin, but since some doubt exists, they were not used in the interpretation of results.

Type III. Inclusions of Type III may be of any shape or orientation. They are found along curving or intersecting planes that are generally unrelated to crystallographic elements of the host. In many specimens they were more abundant than inclusions of Type I. The planes in which they occur appear to be healed fractures, hence the inclusions are probably secondary. They were not considered in this study.

Behavior During Heating

The behavior of the fluid inclusions was similar to that noted in other studies of this sort. In general, one of three things happened when the inclusions were heated —the vapor bubble either shrank and disappeared, expanded to fill the cavity, or faded without appreciable expansion or contraction. Shrinkage and eventual disappearance of the vapor phase was by far the most common type of behavior noted in the inclusions used in this study. More than a thousand inclusions in beryl, garnet, spodumene, quartz and tourmaline showed this "normal" behavior. Nineteen inclusions in beryl showed expansion of the vapor phase when heated, and five inclusions in beryl showed a fading phase boundary. As compared with previous studies (Cameron, Rowe and Weis, 1953), the "abnormal" behavior exhibited by expanding or fading vapor bubbles was much less common in minerals from the Black Hills pegmatites than in those from pegmatites of Connecticut.

One of the most striking features of the results was the wide range of temperatures obtained from some of the crystals. One crystal from the Peerless mine, for example, showed temperatures of cavity filling over a range of nearly 200° C.—this in inclusions identical in appearance and apparent degree of filling at room temperature. At the other extreme, a crystal from the Bob Ingersoll No. 2 pegmatite had a difference of only 9° C. between the highest and the lowest of more than 30 temperature determinations made on different inclusions. No reason for these differences in results could be found.

The minerals examined in the heating stage showed marked differences in their physical properties. Difference in brittleness was the most outstanding characteristic noted, with the more brittle minerals exhibiting a much greater susceptibility to fracturing at all temperatures, particularly below the temperatures at which the cavities were filled by the liquid phase. Quartz was the mineral that gave the most trouble; great difficulty was experienced in finding inclusions that would remain unfractured at sufficiently high temperatures to permit the filling temperatures to be reached. This was true even with slices 3 to 5 mm. thick. Consequently no significant data were obtained from quartz. Tourmaline and garnet are also very brittle and had to be heated very slowly. Much of the tourmaline was dark colored and had to be cut into very thin slices to allow sufficient light transmission for observation, and the thinness of the sections was undoubtedly a factor in its behavior. Most inclusions in tourmaline showed temperatures of filling below 300° C.; fracturing would undoubtedly have been a greater problem if it had been necessary to go to higher temperatures. Garnet was difficult to polish, because of incipient fractures, but comparatively little difficulty was experienced during heating. Spodumene fractured only rarely, in spite of its good cleavage. Beryl gave the least trouble of all. Cavities fractured and leaked very rarely. It was often necessary to heat an inclusion well above its filling temperature, in order to measure other inclusions in the same section, but if the sections were heated at rates of 2 to 4° C. per minute, few inclusions fractured until they were heated 50° C. or more above their filling temperatures, and many were heated 100° above this temperature without fracturing. Beryl, therefore, appeared to be the least brittle of any of the minerals studied.

Composition of Fluids in Inclusions

Attempts to determine the composition of the fluids in Type I inclusions were largely unsuccessful, although indirect evidence was obtained that has a bearing on the problem. The behavior of the fluids throughout a wide temperature range suggests that the liquid in the cavities is aqueous. It has a very low viscosity at all temperatures above its freezing point, as shown by the mobility of the vapor bubbles. Freezing points measured for a few inclusions were found to range from −19° C. to −3° C. It was noted that inclusions with the highest temperatures of vapor phase disappearance also had the lowest freezing points. For example, an inclusion in beryl whose vapor phase disappeared at 465° C. was found to freeze at −19° C., whereas an inclusion in spodumene showed a temperature of disappearance of 260° C. and a freezing temperature of −4° C.

A spectrographic analysis of the fluids was attempted by Prof. V. W. Meloche of the Chemistry Department of the University of Wisconsin, but he was unable to provide a positive identification of any ions in the solutions.

Calculations of hypothetical expansion curves that could be expected from inclusions containing pure water were compared with expansion curves actually measured in some of the long, slender inclusions found in beryl and spodumene. The calculated curves were found to be similar to, but not idential with the measured curves (Cameron, Rowe and Weis, 1953). None of the cavities appear to contain saturated solutions, and none of the inclusions examined showed evidence suggesting that they contained fluids having a critical temperature below that of pure water (374° C.).

All of the above features could be explained if it is assumed that the inclusions contain solutions of water and moderate amounts of soluble salts. The few available analyses of fluid inclusions list NaCl, KCl, and other simple salts, in concentrations as high as 12 per cent (Ingerson, 1947, p. 378), but no analyses of fluids in pegmatite minerals have been made. It is reasonable to suppose that fluids containing simple salts could occur in inclusions in pegmatite minerals, but concentrations of 20 to 40 per cent would probably be required to raise the critical temperatures of the solutions high enough to account for the presence of liquids at 515° C., the highest temperature at which they were observed. Further

TABLE 1.[1] SEQUENCE OF MINERAL ASSEMBLAGES IN ZONED PEGMATITES, BLACK HILLS, SOUTH DAKOTA

	Peerless	Highland Lode	Helen Beryl	Bob Ingersoll #1	Hugo
1. Plagioclase-quartz-muscovite	X	X	X	X	X
1*a*. *	X				
2. Plagioclase-quartz					X
3. Quartz-perthite-plagioclase, with or without muscovite	X	X	X		X
4. Perthite-quartz		X	X	X	
5. Perthite- (or microcline-) quartz-plagioclase-amblygonite-spodumene			X	X	X
6*a*. †Plagioclase-quartz	X	X		X	X
6. Plagioclase-quartz-spodumene					
7. Quartz-spodumene			X		X
8. Lepidolite-plagioclase-quartz				X	
9. Quartz-microcline					X
10. Microcline-plagioclase-lithia-micas-quartz	X				X
11. Quartz					

[1] From Internal Structure of Granitic Pegmatites. Cameron, Jahns, McNair and Page: *Econ. Geology, Monograph* 2, (1949).

* 1*a*—A variant of assemblage 1 is distinguished in the Peerless on the basis of a change in proportions of the essential minerals.

† 6*a*—In which spodumene is not an essential mineral, is considered as a variant of assemblage 6.

X—indicates mineral assemblage recognized in zones.

consideration is given to the question of composition in the section on discussion of results.

RESULTS

The most striking feature of zoned pegmatites is the consistency of arrangement of mineral assemblages from pegmatite to pegmatite and from district to district (Cameron, Jahns, McNair and Page, 1949). Table 1 shows the sequence of mineral assemblages described in the Black Hills pegmatites included in this study and the zones in which they occur. In all cases zone numbers and the mineral assemblages to which they refer correspond to the zone numbers shown on the graphs of temperature determinations.

Results of temperature studies on beryl crystals from three of the twelve pegmatites studied were extensive enough to show trends when plotted in graphical form. In these graphs (Figs. 5, 6, and 7), the zones from which the samples were taken are indicated at the bottom (abscissa), and the temperatures are given on the vertical scale (ordinate). Each dot represents the temperature of disappearance of the vapor phase of one inclusion. All inclusions in beryl that were plotted were of fluid Type I.

Highland Lode (*John Ross Mine*)

The Highland Lode pegmatite (Fig. 5) contains four zones. Beryl occurs in the three inner zones, and primary type inclusions were found in all of the beryl studied. Seven crystals were collected: three from Assemblage 3 (First intermediate), one from Assemblage 4 (Second intermediate), and three from Assemblage 6*a* (Core). One of the crystals in Assemblage 6*a* was very near the center of the core; the other two were near the outside of the core. In the graph they are shown separately as subdivisions of the zone.

Temperature values ranged from 216° to 404° C. Temperatures for the first intermediate zone (Assemblage 3) ranged from 264° to 357° C. The mean temperature for all inclusions in this zone was 313° C. In the second intermediate zone (Assemblage 4) temperatures ranged from 216° to 361° C. However, a group of fifteen inclusions gave values ranging from 216° to 234° C.; although they appeared of primary type, they gave values much different from other inclusions and may represent a special group. The other inclusions from this zone ranged from 276° to 361° C., with a mean of 314° C. Inclusions from the two crystals in the outer part of the core gave temperatures ranging from 254° to 316° C. Their mean temperature was 290° C. Inclusions from the crystal nearest the center of the core ranged from 217° to 402° C., with a mean temperature of 257° C.

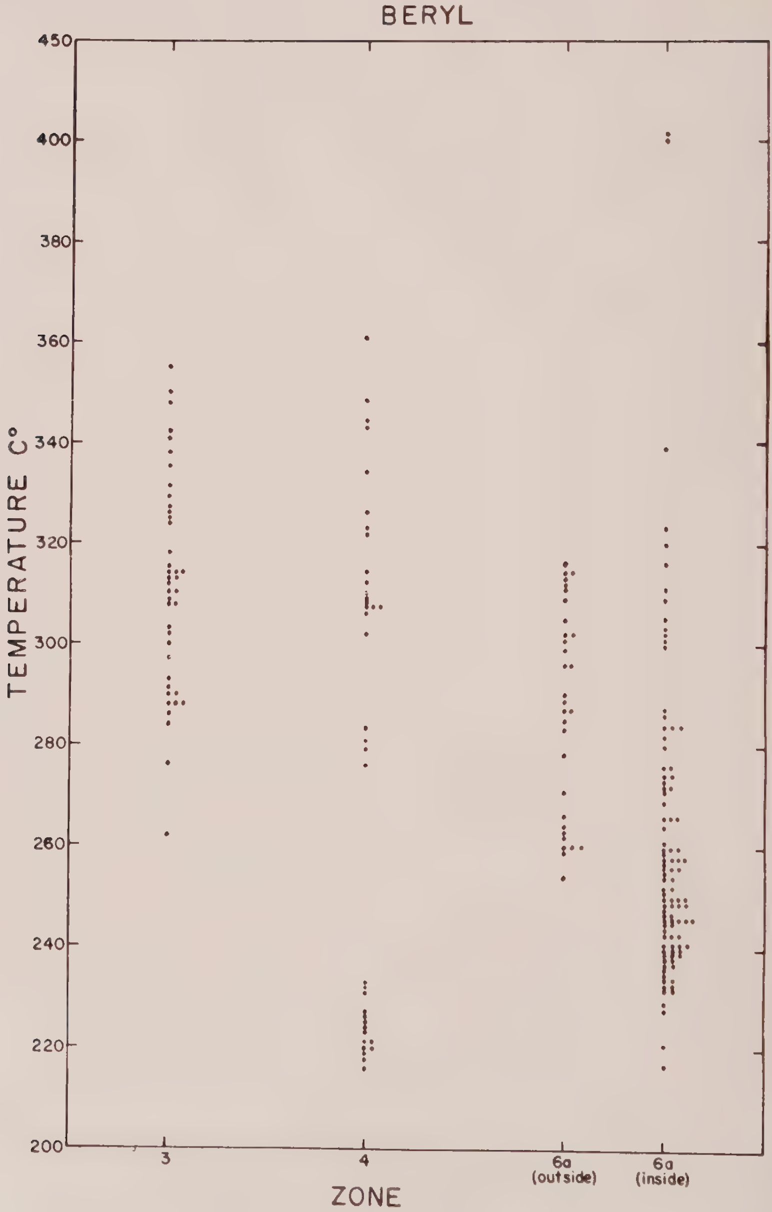


FIG. 5. Temperatures of disappearance of vapor phases in fluid inclusions in beryl. Highland Lode (John Ross) pegmatite, Custer, South Dakota. Each dot represents the temperature of disappearance measured in one inclusion.

Bob Ingersoll No. 1 Pegmatite

The Bob Ingersoll No. 1 pegmatite contains five zones (Fig. 6). Beryl is present in three of these zones, but only samples from the wall and the core contained primary type inclusions. Two crystals from the wall zone (Assemblage 1) gave temperatures ranging from 317° to 515° C., with a mean temperature of 395° C. Two crystals from the core (Assemblage 8) gave temperatures ranging from 308° to 489° C., with a mean temperature of 355° C. Another crystal from the wall zone contained many secondary type inclusions with temperatures ranging from 140° to 200° C. A rounded crystal of beryl from the contact between the third and fourth intermediate zone (Assemblages 3 and 6*a*) contained thousands of negative crystals that give temperatures ranging from 120° to 170° C. Negative crystals from this specimen were somewhat different in appearance from those usually found in beryl. Their corners were commonly slightly rounded, rather than sharp, and the inclusions appeared flattened parallel to one prism face. They appear to be of Type I, but are sufficiently different in appearance to make their classification uncertain, and are therefore not shown on Fig. 6. A crystal from the wall zone contained several negative crystal cavities that appeared to contain the customary two phases, but no change was apparent when heated to 560° C. Observation became difficult at this temperature, and heating was discontinued. No definite behavior pattern was established in this last group of inclusions.

Bob Ingersoll No. 2 Pegmatite

Inclusions of primary type were found in three beryl crystals from the Bob Ingersoll No. 2 pegmatite. One crystal from the wall zone contained four inclusions ranging from 302° C. to 365° C. Two crystals from Assemblage 7 (core) gave temperatures ranging from 290° to 349° C. In one of these specimens, thirty-three inclusions gave temperatures ranging from 341° to 349° C.; the mean of all temperature values from this zone was 335° C.

Peerless Pegmatite

The Peerless pegmatite contains five zones (Fig. 7). Beryl occurs in the outer three; however, the outer two are distinguished only on the basis of variations in the proportions of their mineral constituents, and are in reality subdivisions of Assemblage 1. One crystal from the outer subzone gave temperatures ranging from 257° to 405° C. with a mean temperature of 317° C. Four crystals from the inner sub-zone gave temperatures ranging from 232° to 450° C. The mean temperature from this zone was 359° C. Two crystals from Assemblage 3 gave temperatures ranging

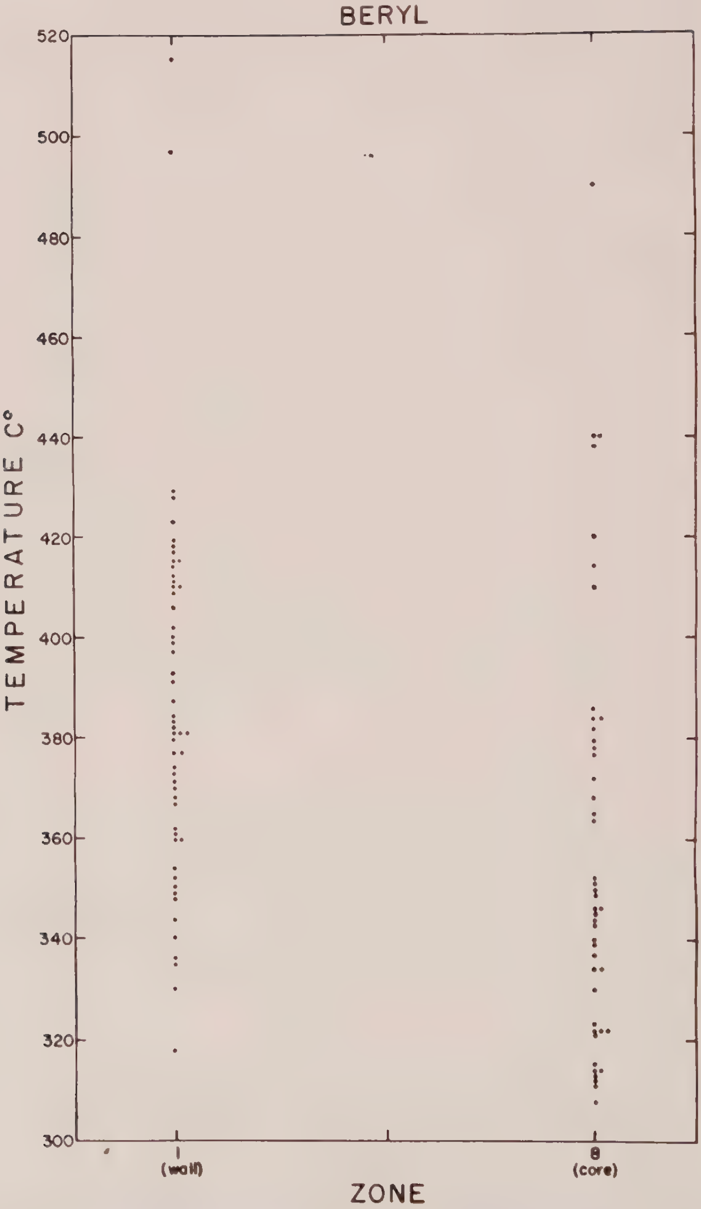


Fig. 6. Temperatures of disappearance of vapor phases in fluid inclusions in beryl. Bob Ingersoll No. 1 pegmatite, Keystone, South Dakota. Each dot represents one inclusion.

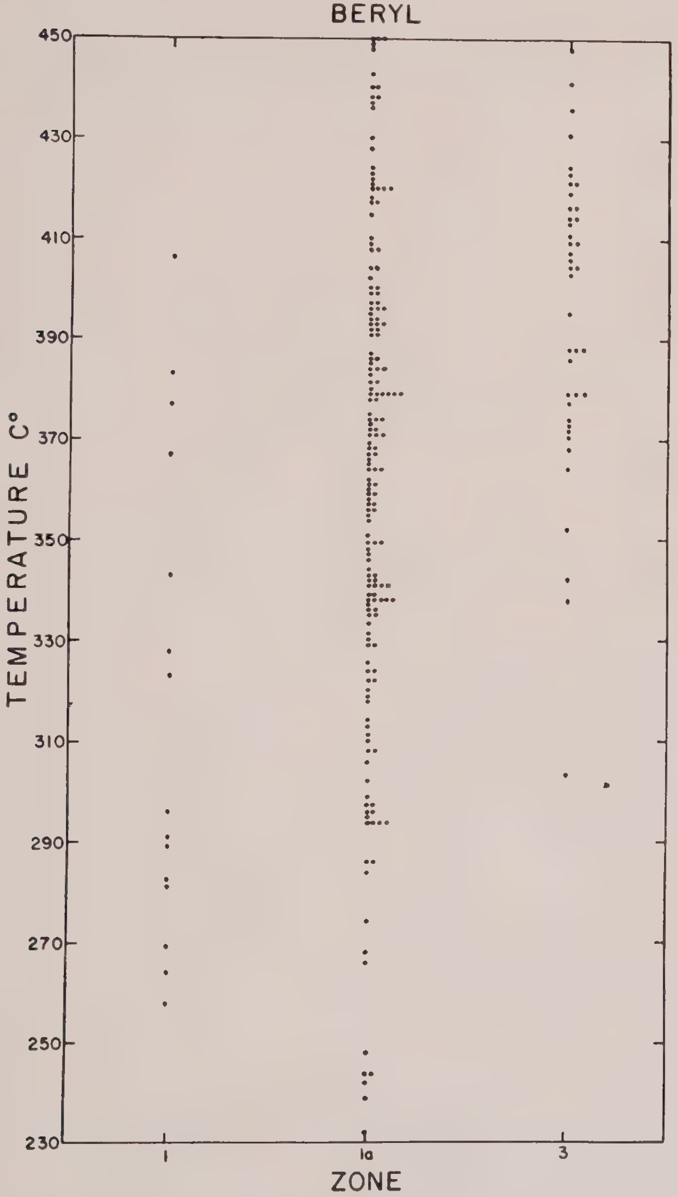


FIG. 7. Temperatures of disappearance of vapor phases in fluid inclusions in beryl. Peerless pegmatite, Keystone, South Dakota. Each dot represents one inclusion.

from 304° to 447° C. The mean temperature was 405° C. A single tapering crystal from the inner sub-zone of Assemblage 1 was 22 inches long and had a maximum diameter of 8 inches. Samples were collected from three points along the outside of the crystal and three points along its core. Temperatures obtained from the outer part of the crystal had a mean of approximately 380° C. and from the inner part, 343° C. No variation from end to end was apparent. Similar measurements on smaller crystals showed no systematic differences.

Hugo Pegmatite

The Hugo pegmatite contains beryl in at least five of its eight zones; however, only one crystal from Assemblage 2 contained inclusions of primary type (Type I). Nineteen negative crystals gave a mean temperature of 328°, with a range of 309° to 353° C.

Tourmaline

Primary type inclusions (Type I) were found in seventeen tourmaline crystals from five pegmatites. They showed no consistent trends from zone to zone. It was noted that the temperature values were always considerably lower than those obtained from beryl from the same pegmatite or from corresponding zones from other pegmatites. Temperatures above 300° C. were found in only three inclusions, from two different pegmatites. The mean temperature for all inclusions in tourmaline was approximately 250° C.

No differences in the appearance of fluid inclusions in tourmaline and beryl were noted. An appreciable difference in the compositions of solutions in the inclusions from the two minerals might account for the contrasting results, but the existence and importance of such a difference cannot be evaluated without accurate chemical analyses of the fluids. Beryl, spodumene and garnet give results that cross-check rather well, suggesting that there may be some characteristic peculiar to tourmaline which accounts for the difference.

Quartz

Two specimens of quartz from the Hugo pegmatite were heated. One of these showed poorly developed negative crystals along a plane that may have been a healed fracture. Fourteen inclusions gave values ranging from 376° to 411° C., with a mean of about 398° C. A second quartz specimen from the Hugo contained disseminated, poorly developed negative crystals. Twenty-four inclusions from that specimen gave temperatures ranging from 383° to 422° C., with a mean temperature of about 400° C.

Spodumene

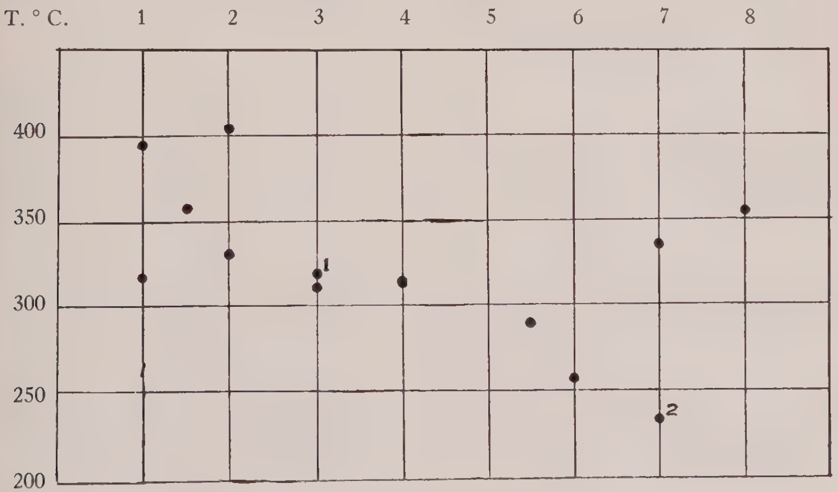
Several fragments of semi-transparent green spodumene were collected from the core of the Helen Beryl pegmatite (Assemblage 7). Rod-shaped inclusions of Type I were very abundant in these specimens. They gave temperatures ranging from 179° to 282° C., with a mean of about 235° C.

Garnet

Two garnet crystals from the second intermediate zone (Assemblage 3) of the Highland Lode gave temperatures ranging from 301° to 342° C. The mean temperature was 318° C. The inclusions were negative crystals in planes parallel to octahedral faces.

The most notable feature of the foregoing results is the broad range of temperatures obtained from individual pegmatites, individual zones, and even from individual crystals. Certain trends are suggested, as in the Peerless, which shows an apparent increase from a mean of 317° C. in the wall to 395° C. in zone 3. The Bob Ingersoll No. 1 gave the opposite trend, with a decrease from 395° in the wall to 355° in the core. The Highland Lode also suggests a downward trend, from 314° in zone 3 to 257° in the center of zone 6*a*. Table 2 summarizes the results in graphic

TABLE 2. PEGMATITE ZONE



1. Garnet, Highland Lode pegmatite.
2. Spodumene, Helen Beryl pegmatite.

Composite results of temperature studies on all pegmatites. Each dot represents the mean of all temperatures in one zone of one pegmatite. Pegmatites include the Peerless, Highland Lode, Helen Beryl, Hugo, Bob Ingersoll No. 1, and Bob Ingersoll No. 2.

form, and shows both the somewhat ill-defined tendency toward decreasing temperatures in inner zones, and the very considerable difference in temperatures from equivalent or adjacent zones of various pegmatites. This great difference in temperatures certainly emphasizes the need for further work and adequate interpretation, if nothing else. Presentation of conclusions based on such variable results is obviously not justified, particularly since there is at present no sure basis for accounting for the wide range of temperatures of the results. However, although no conclussions are justified, certain possible interpretations are implied. To evaluate these, it is necessary to consider the many factors which may influence the results obtained from any one inclusion or group of inclusions.

Discussion

The pegmatites of the southern Black Hills have been intruded into a pre-Cambrian series of complex structure and uncertain age. The pegmatites themselves have been dated by Goodman and Evans (1933). Using the uranium-lead ratio method, they determined that the Bob Ingersoll No. 1 pegmatite was 1,500 million years old.

The country rocks of the area are schists, amphibolites and quartzites. Garnet, staurolite and sillimanite schists predominate. Sillimanite has been recognized in rocks adjacent to most of the pegmatites.

Structural features near the pegmatite contacts indicate that the pegmatitic material behaved as a viscous or plastic mass as it was intruded, and that it was forcibly injected into the country rock under considerable pressure. The schist within several feet of the pegmatites is crumpled and distorted. Induced foliation, rolls and sharp contacts are common. There has been little chemical alteration of the country rock; the only visible change that has taken place is the formation of a tourmalinized zone one to six inches thick in the schist at the contacts of almost all of the pegmatites.

The structural and mineralogic features associated with their contacts suggest that the pegmatites were intruded under considerable pressure but no quantitative data are available. Unfortunately, much of the discussion to follow requires some knowledge of the pressures prevailing at the time of pegmatite intrusion and crystallization, if all of the observations are to be interpreted fully. An attempt is made to interpret the observations in terms of the pressures most probably present, and where possible, maximum and minimum pressures and their effects are indicated.

The primary purpose in most studies of fluid inclusions is to learn the temperature of crystallization of the minerals in which they occur. Sorby, in his original work, dealt principally with minerals presumed to have crystallized from aqueous solutions at relatively low pressures and temperatures, and in his study he made certain basic assumptions that he used to interpret what he saw. It has since been pointed out (Bailey and Cameron, 1951) that in each new study of fluid inclusions, it is necessary to reconsider the seven assumptions that are basic to the method. Each assumption must be evaluated anew, in terms of evidence obtained in that particular study, and an attempt must be made to relate them to each other and to the problem as a whole. The seven basic assumptions are as follows:

1. The fluid exactly filled the cavity at the time of formation.
2. Primary and secondary types of inclusions can be distinguished.
3. The solutions were aqueous; no gases such as CO_2 or H_2S were present.
4. Pressure at time of inclusion was low or can be estimated.
5. No change in ratio of cavity volume to liquid volume has taken place since the inclusions were formed.
6. No gain or loss of material has occurred in the cavity.
7. The sample is representative.

Assumption 1, that the cavity was exactly filled by fluid, is probably correct for all of the inclusions considered in this study. If temperatures were much above 500° C. at the time of crystallization, the inclusions may have been filled by a gas, rather than by a liquid. Whether this is true or not will depend upon the composition of the fluids and the pressure on the system, as well as the temperature of formation, since the presence of dissolved salts will lower the vapor pressure and raise the critical temperature of water. The state of the fluid is unimportant to the method, however; true temperatures of crystallization can be calculated in either case as long as pressure-volume-temperature relationships of the solution, and the pressure at the time of crystallization are known.

If the fluid was included as a gas, it must necessarily have filled the cavity at the time of inclusion. If it was included as a liquid, it would fill the cavity or that part of it which was unoccupied at that time. If a gas was also present, simultaneous inclusion of both phases might take place, but that appears extremely improbable. A solid is present in some of the cavities in spodumene, but it may actually be just an inclusion of spodumene itself; in any event, since the solid particles do not appear to go into solution at elevated temperatures, their presence serves only to decrease the volume of the cavity.

The inclusion of a gas phase and a liquid phase simultaneously would have a much more serious effect, as has been pointed out elsewhere (Cameron, Rowe and Weis, 1953). In some studies of fluid inclusions, such a situation seems possible, but inclusion of a vapor and a liquid phase at the same time in inclusions in Black Hills beryl does not appear likely. The peculiarities in behavior expected if two phase inclusions had formed were not observed. Cavities in beryl from several Connecticut pegmatites have been found to contain CO_2. The presence of at least minor amounts of CO_2 should therefore probably be suspected in all the pegmatites of that district. Visual evidence suggests that neither CO_2 nor any other gases are present in the inclusions in Black Hills pegmatite minerals. It has been found by measurement and calculation that expansion curves of salt solutions lie on one side of the calculated curve for pure water and the expansion curves for water plus CO_2 lie on the other side of the calculated curve. All expansion curves measured in elongate inclusion in Black Hills pegmatite minerals lie on the salt solution side of the calculated curves. The addition of CO_2 or other gases should lower the critical temperature of water; the presence of liquid phases at temperatures as high as 515° C. in inclusions in beryl shows that critical temperatures have been raised. The only set of conditions possible that may have resulted in the inclusion of two phases would be those under which combinations of liquid water and water vapor are present in the system. This appears extremely unlikely. Even moderate pressures would serve to keep concentrated salt solutions in a liquid state. Keevil (1942) has given the vapor pressure of a saturated solution of NaCl in water at 500° C. as 318 atmospheres; saturated KCl and water at 500° C. has a vapor pressure of only 204 atmospheres. Pure water at 500° C. requires a pressure of about 690 atmospheres to maintain its critical density (the density of liquid water at its critical temperature, 374° C.). The minimum and maximum pressures are therefore 204 and 690 atmospheres, and the solutions in the inclusions, if the compositions are inferred correctly, must have vapor pressures somewhat between these limits. In the absence of more precise data, a pressure about halfway between the two extremes (450-500 atmospheres) should give at least an approximation of the proper magnitude. One mile of rock cover (specific gravity 2.7) can exert a lithostatic pressure of 420 atmospheres; it would appear probable that pressures in excess of that equal to two miles of rock cover would be ample to account for the observed behaviors of all of the inclusions. Such pressures are quite in keeping with the geologic occurrence of the pegmatites, and they might conceivably have been two or three times higher. As temperatures dropped during the crystallization of the pegmatite, pressures could be expected to remain fairly constant, thereby maintaining the fluids in a liquid state throughout the range of crystallization. Even if pressures were not constant, a lowering of pressure to the point where it would equal the vapor pressures of the fluids would result in the instantaneous formation of a vapor phase, and the inclusions would again consist of only one phase. Features within the pegmatites do not appear to favor the assumption that pressure changes of considerable magnitude took place during crystallization. Although crystallization might be expected to reduce the volume of the pegmatitic material somewhat, any significant thickness of rock cover would probably exert enough pressure to take up all of the "slack" formed in this way, maintaining original pressures with little change. If the rocks surrounding the pegmatites had sufficient ridigity to resist external pressures, the pressures inside the pegmatites might be greatly reduced, but the extent and the plastic nature of wall rock deformation indicate that wall rocks were not at all rigid.

Fluctuations in pressure due to external forces appear equally improbable. No evidence of post-intrusive deformation has been seen in the pegmatites; furthermore, large unfractured crystals are not likely to grow in an environment characterized by fluctuating pressures and the structural disturbances that would probably accompany them. The laws of probability appear to favor the interpretation that the fluids were in a liquid state when they were included in the cavities, unless both pressures and temperatures were substantially below the minimum figures listed above, as they might have been if they were the result of hydrostatic, rather than lithostatic load. The possibility of higher pressures and temperatures is discussed in a section below.

Assumption 2, that the inclusions are primary, is considered above. All visible criteria indicate that Type I fluid inclusions are related to primary crystallographic features, and that they bear no relationship to recognizable secondary features. On the basis of visual criteria, Type I inclusions represent the only group likely to be primary.

The third assumption, that the solutions are aqueous, has been answered in part. Behavior of the fluids at various temperatures, measurements of freezing temperatures, the presence of a liquid phase at temperatures up to 515° C., limited information on analyses (Ingerson, 1947, p. 378), the low viscosity of the solutions, and the expansion curves actually measured, can all be best explained by the known properties of dilute solutions of simple salts in water. No other liquids that are likely to occur in pegmatites are known to have this combination of physical and chemical properties. Concentration of some of the solutions, at least, must be fairly high, since the critical temperature of a 10% KCl solution is 435° C. and 81 inclusions in beryl were observed to contain a liquid phase at temperatures between 450 and 500° C. It is hardly possible that the fluids are saturated at 500° C.; this would result in such a marked degree of supersaturation at room temperatures that crystallization of salts would be almost certain to occur. (Water at 25° C. is saturated by 26.5% KCl.) The presence of CO_2 is not indicated by the behavior or the expansion curves of the liquids. More soluble gasses might be present in the cavities, provided they do not constitute a sufficiently large proportion to cause a significant variation in the expansion curve of the solution, but the presence of soluble gas in the inclusions has not been detected.

Sorby's original paper on fluid inclusions assumed that they represented samples of the mother liquor from which the mineral crystallized. The apparent composition of the fluid inclusions in beryl are quite different from the composition of the mother liquor which many geologists visualize as having produced pegmatites. It may be possible that small quantities of water, containing various concentrations of the more soluble salts, were present in the original parent material as immiscible droplets.

Another possibility is suggested in a paper by Raistrick (1949, p. 360), who describes a melt of sodium trimetaphosphate from which crystals were being grown. He states that bubbles of what was believed to be moisture were formed at the surface of the growing crystals. An analogous process is plausible; crystallization of anhydrous pegmatite minerals might cause water droplets to form as local concentrations at the growing crystal face, and some of them might become trapped in cavities as the crystal continues to grow. The concentration of water in solution might be variable over short distances; this, together with local variations in rates of crystallization might in turn cause variations in the amount of water formed locally, and thereby account for the erratic distribution of the fluid inclusions. Their abundance, and the availability of highly soluble salts such as KCl and NaCl for solutions, might also vary locally as a result of factors only indirectly related to the crystallizing mineral and its composition. These ideas belong to the realm of speculation at present, but they appear to be possible, and further work may add information as to their validity.

Inclusions formed in this way would be perfectly valid indicators of crystallization temperatures, even though they did not represent a sample of the parent fluid from which the crystals formed. Sorby's original idea is none the less sound, however. In many minerals one would expect that a sample of the parent fluid could be entrapped and preserved. If pegmatites crystallize from true igneous melts, such a sample should now consist of either a glass with a composition near the average composition of the pegmatite, or a heterogeneous mixture of small crystals, including at least the commoner and more abundant minerals found in the pegmatite. It may be that inclusions of this type actually exist; many pegmatite minerals contain fine-grained inclusions of unknown composition that may be true samples of the fluid from which the pegmatites grew. Certainly they justify further investigation as a check on that possibility.

Assumption 4, that pressure at the time of crystallization was small (that is, not far above the vapor pressure of the solution) or can be estimated, has been considered in part in a preceding section. It is undoubtedly one of the most difficult, as well as one of the most important assumptions to answer. It has been shown that pressures in excess of 400 atmospheres were almost a certainty if a liquid state is to be maintained at 500° C., as it was in a few of the inclusions; thus we have a fairly reliable lower limit for pressures during crystallization. The establishment of an upper limit for pressures is a much more difficult matter. There is no evidence of any kind that provides conclusive information, although all of the geologic features associated with the pegmatites are compatible with the idea that pegmatites formed at a considerable depth. Deformation of wall rock by intrusion, formation of thin tourmalinized zones in the wall rocks at the pegmatite contacts, association of the pegmatites with rocks of medium to high metamorphic grade, the size of the pegmatite crystals, suggesting a stable, deep-seated environment during cooling, all could be explained by crystallization at depths up to 10 miles or more, but none of these features necessarily requires such depths. It has long been postulated that volatile constituents concentrated in the rest magma are responsible for the giant crystals in pegmatites. Presumably these volatiles are held within the pegmatitic fluid until crystallization is complete, and this might require considerable pressure—but how much pressure? Unfortunately, neither geologic history nor visible features provide a useful answer. The fact that deformation of the wall rocks as a result of intrusion was by folding and recrystallization, rather than by fracturing, appears to favor a substantial depth, but the rest of the features could have formed over a wide range of pressures. The only upper limit for pressure is that point at which metamorphism of the pegmatites themselves would begin, and that point has never been satisfactorily established.

Assumptions 5 and 6 can be considered together. The possibility of change in cavity volume has been discussed by others, and is not important in the temperature range that we are concerned with. No evidence of deposition on the insides of the cavities was seen, but if additional beryl was deposited, it probably could not be detected. The amount of beryl likely to have been deposited from an aqueous solution, even at high temperatures, is not likely to have much effect on the magnitude of the results. The change in cavity volume—liquid-volume ratio through the gain or loss of material from the cavity is a different matter. Kennedy (*Econ. Geol.*, 1950, p. 543) cites work by Grunig which shows that water under pressures of 1500 atmospheres and at a temperature of 150° C. can be forced into inclusions in fluorite. The probability of diffusion of material in or out of inclusions in beryl appears to be much less, however. Liquid CO_2, which would exert a pressure of nearly 70 atmospheres at room temperatures, has been described in beryl from Connecticut (Cameron, Rowe and Weis, 1953) and pressures of that magnitude, applied over a long period of time, should cause some migration of material out of the cavities if migration of ions or molecules was possible. Apparently the space lattice of beryl is not sufficiently "porous" to permit such change to take place.

Leakage was noted in a number of specimens as they were being heated. Quartz gave the greatest difficulty in this respect, but even beryl was seen to fracture in a number of specimens. Fracturing and leakage at some time during the geologic past also remains a possibility. The behavior of the fluids in the inclusions does not favor this possibility. Leakage would be expected to reduce the density of the fluids in the inclusion, and this, in turn, would result in a larger vapor bubble and higher temperatures of disappearance, up to a certain point, but if more liquid was lost, the vapor-liquid ratio would alter enough to cause the liquid phase to shrink and disappear or to fade and disappear as it is heated. Behavior of these types was extremely rare; only 24 of more than 1100 inclusions showed shrinking or fading liquid phases. It is very unlikely that many of the cavities leaked just enough to cause high disappearance temperatures, yet so few leaked enough to cause the unusual behaviors. Similarly, the addition of material to the cavities is not indicated. Additional material might be expected to give low temperatures, whereas temperatures tended to be high.

Assumption 7, that the sample is representative, must be answered from each crystal, zone and pegmatite studied. The results shown in Fig. 7 for Zone 1 in the Peerless pegmatite, for example, are probably not significant. Fifteen inclusions, that gave results covering a range of 150 degrees, are of questionable significance indeed, although comparison of the results with those from the adjacent Zone 1*a*, in which 174 inclusions were measured, shows fairly good agreement in range, at least. However, the necessity of compiling a large volume of data cannot be overemphasized. Of the pegmatites described in this study, the writer feels confident that only one, the Highland Lode pegmatite, has been adequately sampled and studied. The others have trends that are suggestive, but subsequent work might modify those trends considerably, and more data are definitely needed. Unfortunately, a study of this type is tedious and time-consuming, and not all pegmatites, nor all crystals, contain visible primary type inclusions. In addition, the complexities of behavior and interpretation demand the most careful observation; the problems are numerous enough even when all possible data has been gathered.

INTERPRETATION

Temperature zoning

In view of the many uncertainties involved in the evaluation of the assumptions, it is obvious that no definite interpretations of the results are possible. Despite the difficulties, however, certain aspects of the results require some comment. It must be kept in mind that the objective of this section is not to present conclusions; many of the ideas presented are highly speculative, and are intended only to provide suggestions that may serve as useful guides in the course of further work of this type.

The original objective of the study was to determine whether temperature zoning existed in correspondence with mineral zoning. Only one pegmatite yielded abundant data for more than two zones. This pegmatite, the Highland Lode mine, contained four zones, and inclusions were measured in three zones (Fig. 5).

Interpretation appears simple if the mean temperature of each zone is considered. The outermost zone for which data was obtained had a mean temperature of 313° C., the next zone 314°, the outer part of the core 290° and the inner core gave a mean temperature of 257° C. Results from the outer zone may be incomplete. However, the difference between the highest and lowest mean, even considering the inner part of the core as a separate unit, is only 107° C., whereas the differences between the highest and the lowest temperatures measured in each zone are 93°, 85° (for the upper group), 62° and 185°, for zones 3, 4, 6*a* (outside), and 6*a* (inside), respectively. Thus the range of temperatures measured in individual zones has a magnitude comparable to the difference between the highest and lowest mean.

Although no explanation can be offered to account for this wide range of temperatures formed in individual zones or in individual crystals, the writer feels that the existence of a trend toward lower mean temperatures nearer the core may be significant, and that it may be explained by decreasing temperatures during crystallization. However, this apparent trend was found in only one pegmatite, and is hardly sufficient to prove the original hypothesis. It appears to support the hypothesis, *in this particular pegmatite.*

The Peerless pegmatite near Keystone, yielded extensive data from only one zone, but the mean temperatures from the three zones studied suggest an increase in temperature from the walls inward (Fig. 7). This may be due in part to insufficient data, but the geologic history of the pegmatite also undoubtedly plays an important role. The Peerless pegmatite is a complex body, consisting of at least two, and possibly three limbs. Detailed study by the U. S. Geological Survey has shown that it was very probably formed as a result of two or more separate intrusions, and this complex history may account for the trends that appear to contradict the results found in the Highland Lode.

Table 2 summarizes in composite form the results from all of the pegmatites. Each dot on the table represents the mean of all temperature determinations from one zone in one pegmatite. It will be noted that no clear-cut trend toward decreasing temperatures in the interior of the pegmatites has been established. Obviously, much more data, from many more pegmatites, is desirable.

Temperatures of crystallization

The determination of true temperatures of crystallization is not a necessary prerequisite in the recognition of temperature zoning, as long as the relative differences in temperature are known. It is of interest, however, to see how far the interpretation of results can be carried, and how much information they can provide in determining the true tem-

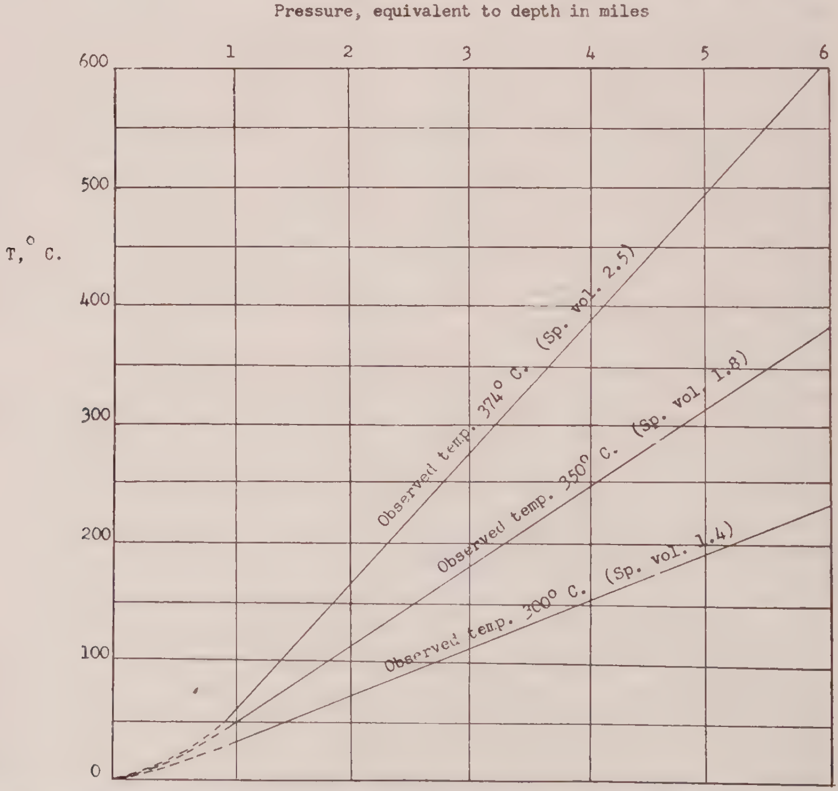


FIG. 8. Curves showing temperature to be added to observed temperature of disappearance of vapor phase. Corrections are for inclusions containing pure water.

peratures of pegmatite crystallization. To do this requires an estimate of the pressures that existed at the time of crystallization, and a knowledge of the pressure-volume-temperature relationships of the fluids in the cavities.

It appears likely that pressures were equivalent to the weight of a column of rocks between 1 and 10 miles thick (420 to 4200 atmospheres). The compositions of the fluids in the inclusions are imperfectly known, and practically no pressure-volume-temperature information is available for salt solutions. The only accurate pressure-volume-temperature data available are for pure water, and that, therefore, constitutes the only source of information useful for predicting behavior.

Figure 8 gives pressure corrections required for inclusions containing pure water. Similar correction curves for salt solutions cannot be calculated from data now available, but since their vapor pressures are lower, the corrections for pressure will almost certainly be greater for salt solutions than for pure water. The significance of the curves in Fig. 8 lies in the fact that a moderate increase in observed temperatures of disappearance results in a marked increase in the size of the correction required, making the relative differences between high and low observed temperatures much greater. Perhaps if the pressure corrections could be applied with assurance to the results presented in this paper, the differences between temperatures observed in the various zones would be more clear-cut, and the evidence for temperature zoning might be somewhat stronger. Although none of the evidence is conclusive, the writer feels that pressures at the time of formation were at least the equivalent of two miles of rock cover. Inclusions giving observed temperatures in the 400–500° C. range would therefore probably require corrections of at least 200 to 300°C. Evidence from fluid inclusions thus appears to indicate that pegmatites may have begun to crystallize at temperatures as high as 600 to 800° C. These figures are put forth purely as a tentative hypothesis, subject to revision in the light of further investigations, and they should not be accepted until abundant supporting evidence of a more precise nature is available.

Summary and Conclusions

The original objective of the study was to determine whether temperature zoning existed in correspondence with mineralogical zoning in pegmatites. This objective was not achieved. Only one pegmatite, the Highland Lode, provided adequate data, and while a trend toward decreasing temperature in interior zones is suggested, the wide range of temperatures measured in each of the four zones makes the validity of the interpretation questionable.

The results have also shed some light on the possible range of temperatures at which pegmatite crystallization took place. Actual measurements ranged from 216° to 515° C. Although pressure corrections cannot be accurately estimated, a pressure correction of only 400 to 800 atmospheres might add as much as 200 to 400° to these values, and place them in the same range as might be expected in crystallizing granites. Even though temperature estimates are necessarily more qualitative than quantitative, the results appear to indicate that temperatures were high—higher, at least, than earlier fluid inclusion studies have indicated.

The need for much more information has been demonstrated throughout the course of the investigation. It is necessary to have a more accurate basis for evaluating the many possible sources of error, particularly those related to pressures at the time of crystallization, composition of the fluids, and the pressure-volume-temperature relationships of the fluids. The possibility that material has been added or subtracted from the cavities needs further study. The significance of the wide range of temperatures measured in individual crystals and individual zones must also be determined.

Several lines of investigation have been brought to light that may yield important dividends to future investigators. If they are carried out, their results may be expected to add considerably to our knowledge of the history of pegmatite crystallization. Fine-grained, heterogeneous solid inclusions merit attention as possible samples of the original pegmatitic parent material. Accurate quantitative chemical analyses of the fluid inclusions are badly needed. When they have been made, a study of the pressure-volume-temperature relationships of the fluids should be undertaken. Such studies would be of tremendous assistance in the interpretation of existing data and any additional data made available in the future. Studies of fluid inclusions should be continued, in as many pegmatites and as many localities as possible, to accumulate more information of the type presented here. Such studies may unearth valuable information bearing on interpretation, as well as providing more data on the temperatures themselves.

The fact that dissolved salts have the effect of lowering vapor pressure and raising the critical temperature suggests the possibility that many deposits now believed to be pneumatolytic may actually be hydrothermal. This concept appears to be worthy of investigation.

Acknowledgments

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A CLASSIFICATION OF THE 2:1 CLAY MINERALS

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Abstract

A classification of the 2:1 clay minerals is presented in which the per cent of the total replacement which occurs in the octahedral and tetrahedral sheets is considered to be of primary importance. The secondary division is based upon the degree of expansion and the nature of the external cations.

Introduction

During a study of the potassium bentonites from the Ordovician limestones of Pennsylvania (Weaver and Bates, 1951) additional evidence was found indicating that the differences between illite and montmorillonite are not as great as is commonly supposed. Bradley (1944) found that many of the illite-like clays such as glimmerton, bravaisite, Grundy illite, metabentonite, and some glauconites contain expanded layers. Nagelschmidt (1944) found that when illite is treated with $CaCl_2$, portions of the non-expanded layers expand. White (1950) has shown that by treating illite with $MgCl_2$ and precipitating the exchanged potassium the illite expands and gives a montmorillonite *x*-ray pattern. It is thought that many of the montmorillonite minerals, particularly beidellite, contain some non-expanded layers which are indicated by the presence of potassium in the chemical analyses. Caillère and Hénin (1949) have shown that by boiling montmorillonite in KOH the 001 spacing shifts to the 10 Å value characteristic of illite. Barshad (1948) has shown that biotite will exchange K for Mg and form an expanded lattice with a value greater than 10 Å. Many soils scientists have shown that K can be "fixed" by montmorillonite and recently Mortland and Gieseking (1951) caused both montmorillonite and hectorite to collapse to 10 Å by placing them in a solution of K_2SiO_3 and drying at 110° C. Kunze (1952) was able to collapse several 14 Å soil vermiculites to 10 Å by drying them from a solution of $K\ C_2H_3O_2$.

These findings suggest that the same fundamental 2:1 layers can form either an expanded or a non-expanded clay and that it is relatively easy to change the state of expansion. It is proposed that the existence of an expanded or a non-expanded lattice is dependent upon the cations in interlayer positions rather than upon the composition of the 2:1 layers in the lattice and that the type of cation present is independent of the composition of the layers.

The ideas formulated above are illustrated by the illite-montmorillonite groups of minerals and are further supported by studies of K-bentonites.

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ILLITE VERSUS MONTMORILLONITE

General

Three criteria provide the fundamental means of differentiating between the illite and montmorillonite clay groups. Naturally all three were developed from a study of many clays. However, it is significant that the great majority of montmorillonites investigated are those formed from volcanic ash, usually of Cretaceous or Tertiary age. The majority of the illites described in the literature have been found in the Carboniferous sediments. Clays of either type from other sources often do not possess the properties which are diagnostic of the "type" materials. The criteria referred to are as follows:

1. Illite, as usually defined, has a non-expanded lattice, with a *c*-spacing of 10 Å. Montmorillonite has an expanded lattice, 12 to 30 Å in the direction of the *c* axis.

2. Illite commonly gives a hydroxyl-endothermal reaction in differential thermal analysis curves at 500–600, whereas the montmorillonite reaction usually occurs at 600–750° C.

3. Except for the external cations K, Na, Mg, and Ca, the structural formulas of illites and montmorillonites are similar, and in many cases identical. The predominance of K as an external cation is characteristic of illite.

X-ray Data

Probably the most widely used and most reliable means of identifying the minerals of these two clay groups is by *x*-ray diffraction. When a 10 Å value for the first 001 spacing is obtained the clay is considered to be non-expanded and is called illite. If the *x*-ray line has a value of 12 Å or greater, the clay is considered to have an expanded lattice and is called montmorillonite (assuming it is not vermiculite or chlorite).

However, recent laboratory work has shown that the degree of expansion and hence the basal spacings of illite, montmorillonite and many other 2:1 minerals can easily be changed by varying the type of external cation. Table 1 lists some of the 2:1 minerals which have been altered, the original 001 spacing, the physical or chemical treatment and the resulting 001 spacing. It is apparent that by proper treatment the external cations in the expanded 2:1 minerals can be replaced by K and the resulting clay will be of the non-expanded variety. In addition a wide variety of non-expanded 2:1 minerals can be made to expand by replacing the external K by more highly hydrated cations. In the case of the Na based mica, paragonite, it is necessary only to grind the material to clay size in order for it to expand.

TABLE 1. VARIATIONS PRODUCED IN 001 SPACINGS

Author	Original Material	Original 001 Spacing in Å	Treatment	Time	Final 001 Spacing in Å
Nagelschmidt (1944)	Illite	9.7–11.4	Soaking in $CaCl_2$	5 weeks	9.7–12.5
Barshad (1948)	Biotite	10.29	$<1\mu$ material leached with $MgCl_2$	3 months	14.47
Barshad (1950)	Paragonite	9.7	After grinding to $<0.5\mu$		14.3
White (1950)	Illite	10.0	Soaking in $MgCl_2$		14.0
Caillère and Hénin (1949)	Montmorillonite Nontronite	? ?	Boiling in KOH Boiling in KOH	32 hours	10.2 10.0
Barshad (1948)	Vermiculite	14.33	Leaching with $KC_2H_3O_2$	10 days	10.42
Nortland and Gieseking (1951)	Montmorillonite Hectorite	13.15 14.72	Drying from K_2SiO_3 solution		9.90 10.09
Kunze (1952)	Vermiculite	14.0	Boiling in $KC_2H_3O_2$ solution	10 minutes	10.0
Weaver and Bates (1951)	Mixed layer	10.9	Wetting and drying from KOH solution	15 times	10.1

This evidence would indicate that the 001 spacing of the 2:1 layer lattice silicates and therefore their state of expansion is independent of the composition of the 2:1 lattice and depends only upon the type of external cation present.

Differential Thermal Analysis Data

An examination of the differential thermal data shows that the characteristic hydroxyl-endothermal reaction of illite occurs between 500 and 650° C.; however, this figure is determined largely from samples obtained from the Carboniferous rocks. When illites from totally different sources are examined it can be expected that this range will be extended; this is indicated by the Ballater illite described by MacKenzie, Walker, and Hart (1949). The hydroxyl-endothermal reaction of this material occurs at 713° C.

The majority of the montmorillonites derived from the Cretaceous and Tertiary ash beds have a hydroxyl-endothermal reaction which is restricted to a 650–700° C. range. However, Mg and Fe montmorillonites from varied sources extend this range down to 500 and up to 800° C.

It is generally believed that the temperature of the hydroxyl-endothermal reaction is controlled largely, if not entirely, by the various cations in the octahedral layers. As the range in temperature of this reaction for the two clays is almost identical, it would appear that the composition of the octahedral layers varies within the same limits.

Chemical Composition

As is suggested by the temperatures of the hydroxyl-endothermal reaction, the chemical analyses indicate that the octahedral layers for illites and montmorillonites are quite similar and in many cases the same in composition.

The composition of the tetrahedral layers in the clays of the two groups can be indicated only by chemical analysis. Although the ranges of the percentage of aluminum replacing silicon overlap to a considerable extent, the available analyses (largely of bentonites) indicate that many of the montmorillonites have a very small amount of aluminum in the tetrahedral layer, as compared to the known illites. However, this does not mean that a 2:1 lattice with little aluminum in the tetrahedral layers cannot attract potassium and form a 10 Å lattice. It is simply more probable that the potassium was never available. Neither is the converse true. For, even if there is 15 to 20 per cent replacement in the tetrahedral layer but no potassium is available, the lattice will be expanded. This can easily be appreciated by a study of the data presented by Ross and Hendricks (1945). In 25 of the 82 dioctahedral montmorillonites analyzed, nearly 15 percent or more of the silicon ions in the tetrahedral layer are replaced by aluminum. Using a classification based on the chemical composition of the impure pyrophyllite lattice these 25 clays would be referred to as illites whereas on the basis of their degree of expansion they would be called montmorillonites. The fact that expansion is unrelated to the amount of replacement in the tetrahedral layers is further indicated by the work of Barshad (1950) which showed that when the Na mica, paragonite, which has approximately 25 per cent replacement in the tetrahedral layer, is ground to less than 0.5 microns in size it will expand.

Case of the K-bentonites

An excellent example of the similarity of expanded and non-expanded dioctahedral 2:1 clay lattices is shown by the K-bentonites (Weaver and Bates, 1951).

An *x*-ray study of several samples of K-bentonite revealed that the material is composed of randomly interstratified layers of expanded and non-expanded dioctahedral 2:1 clay minerals (montmorillonite and illite) in the ratio of 1:4.

This ratio was determined by varying the extent of expansion of the expanded layers by treating the clay with a variety of cations. When the expanded layers were reduced to approximately 12 Å by substituting K, Na, and NH_4 as the external cations the resulting 001/001 value was 10.3 Å. When the expanded layers were increased to 14-15 Å by treating the clay with H and Ca the 001/001 value was increased to 10.9 Å. When expanded to 17 Å with ethylene glycol the 001/002 value occurred at 9.5 Å. Using the curves computed by Brown and MacEwan (1950) the ratio of 1:4 was determined.

When the mixed layer clay was alternately wetted and dried in a KOH solution the expanded layers were reduced to nearly 10 Å and the resulting 001/001 value for the clay was 10.1 Å indicating that most of the clay was in a non-expanded state.

The differential thermal curves of these mixed layer K-bentonites contain only a single hydroxyl-endothermal peak at approximately 700° C. (A 600° C. peak due to chlorite is sometimes present.) The presence of this single peak indicates that the composition of the octahedral sheets of the expanded and non-expanded layers are similar if not identical.

The structural formula of a K-bentonite sample is:

$$K_{.64}\frac{Ca}{2}{}_{.10}Na_{.02}Mg_{.02}$$

$$(Al_{1.64}Fe_{.02}Mg_{.34})(Al_{.45}Si_{3.55})O_{10}(OH)_2.$$

The K is probably present in the non-expanded layers, whereas the Ca, Na and Mg are held on the expanded layers. This relationship is indicated by the fact that K forms 80% of the total external cations and the *x*-ray data reveals that 80% of total clay layers are non-expanded.

This data on the mixed layer K-bentonites indicate that the compositions of the expanded and non-expanded lattices are similar, that the amount of non-expanded layers is directly related to the amount of K present, and that by supplying more K in the proper manner the clay can be transposed into the non-expanded (illite) type.

NEED FOR NEW APPROACH

The above discussion suggests that in any given impure pyrophillite-talc structure, an expanded or a non-expanded lattice is obtained depending upon the external cations attached to it. The hydroxyl-endothermal reaction occurs at a variety of temperatures, depending upon the composition of the octahedral layers, and does not show any correlation with the *c* dimension.

Although throughout the complete range of impure pyrophillite-talc compositions, either an expanded or a non-expanded lattice can be formed under a variety of conditions, there appear to be compositional poles where one type is predominant. These poles may be the result of three factors: (1) selected sampling in age, location, and variety of source rock, (2) the tendency of certain cations to occur together in nature and, (3) the limited stability of certain combinations of exchangeable cations with cationic substitutions in the lattice.

It is believed that the present poles are primarily due to the first factor. As more clays are described and these poles become less sharply, rather than more sharply, defined, the question arises as to whether these clays should be divided into separate mineral groups when the distinction apparently rests entirely upon the type of external cation present, and particularly when minerals of these groups frequently occur interstratified. It is believed that such a division is not a self-perpetuating concept because it is based upon criteria resulting from modifying processes acting upon the clay, rather than upon the more fundamental composition of the impure pyrophillite-talc structure which reflects more accurately the original composition of the clay and of the source material.

PROPOSED CLASSIFICATION

The result of over-emphasizing the importance of the expandability of 2:1 clays had led only to confusion which increases geometrically as more information is acquired. The author believes that the idea of expandability must be made of secondary importance and all 2:1 dioctahedral and trioctahedral clays treated as one group, with a breakdown into varieties based on chemical composition of the impure pyrophyllite-talc lattice. The terms expanded and non-expanded (or K, Ca, Mg, etc.) can be prefixed to the variety names to indicate the external cations present. At this stage in the development of clay mineralogy it is considered best to use a classification based on hypothetical end members that will include all 2:1 clay minerals.

Table 1 shows how all dioctahedral and trioctahedral 2:1 minerals with varying degrees of expansion can be organized into a compact classification.

Degree of Expansion	Ex. Cat-ions	Per Cent of Total Replacement in 2:1 Lattice								
		>75% in Tetrahedral			>25 and <75% in Both			>75% in Octahedral		
		Tetrite			Tetoctrite			Octrite		
		Dioctahedral		Tri.	Dioctahedral		Tri.	Dioctahedral		Tri.
		Al	Fe	Mg	Al	Fe	Mg	Al	Fe	Mg
Expanded	Ca Na Mg									
Expanded & non-expanded	Ca Na Mg K									
Non-expanded	K									

TABLE 1. CLASSIFICATION OF THE 2:1 CLAY MINERALS

Primary Division

The main breakdown of the 2:1 clay minerals is based upon the location of the replacement in the impure pyrophyllite-talc lattice. Clays having greater than 75% of the total replacement (of cations of a greater charge by cations of a lesser charge) occurring in the tetrahedral sheets are referred to as tetrites. Clays having greater than 75% of the total replacement occurring in the octahedral sheet are called octrites. Clays having greater than 25% of the total replacement occurring in both types of sheets are called tetoctrites.

Each of these sub groups is further divided on the basis of whether the clay is dioctahedral or trioctahedral. The dioctahedral clays are divided into Al and Fe depending upon which is the predominant element in the octahedral sheets. The trioctahedral clays contain Mg (Zn and others are rare) as the predominant element in the octahedral sheets.

Secondary Division

The secondary division is based upon the nature of the external cations and therefore the degree of expansion. The expanded clays have Ca, Na and Mg, etc., as the external cations. The non-expanded clays have K. Clays having both kinds of external cations are of the mixed layer type containing both expanded and non-expanded layers.

TERMINOLOGY

Eventually names might be given to all possible combinations of the two divisions; however, for the present it is believed that the use of descriptive terms will help to avoid confusion. The illite-like minerals are referred to as non-expanded Al 2:1 clays. Where the composition is known they can be further defined and called non-expanded Al tetrites or KAl tetrites, and non-expanded Al tetoctrites; glauconites are non-expanded Fe tetoctrites; trioctahedral illites are non-expanded Mg tetoctrites. Many of the montmorillonites are expanded Al octrites or Ca, Na, Mg., etc., Al octrites; most nontronites are expanded Fe tetrites. Beidellites and other mixed layer minerals are classed as expanded and non-expanded Al tetrites or tetoctrites, or, for example, as CaKAl tetrites or tetoctrites.

CONCLUSION

It is thought that this arbitrary breakdown on the basis of the location of the predominant replacement in the lattice, will avoid the confusion caused by trying to classify newly described minerals by comparing them with established species. From the name the general composition of the impure pyrophyllite-talc lattice and the state of expansion can be inferred. And by making the state of expansion secondary and independent of composition of the impure pyrophyllite-talc lattice a more realistic approach to the origin and genesis of these clays can be used. The composition of the 2:1 lattice reflects the original source of the clay mineral. The composition of the external cations, and degree of expansion, reflects environment and environmental changes occurring during and after formation of the clay. Using this classification it is possible to apply a descriptive name which is based upon the amount of information available rather than a general name which implies much more than is actually known about the clay mineral.

It is realized that this classification may be incorrect and that eventually it may be found that the total amount of excess charge occurring in the 2:1 lattice, or some other factor, is the controlling force in expansion. However, it is believed that this classification is consistent with present data and that it is a pragmatic tool that can be used as a clarifying agent.

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PURIFICATION AND PROPERTIES OF MONTMORILLONITE

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Abstract

Descriptive mineralogical data have been obtained on ten montmorillonites from bentonite deposits located in the United States and Canada, using thermal, x-ray, electron, and chemical methods.

The montmorillonites were hand-picked and subsequently mechanically purified by settling and supercentrifugation. After purification cristobalite was detected in four of the ten samples. Lepidocrocite and hydrous mica were present in one sample. The differential thermal analysis curves show endothermic peaks at (140–160° C.), (650–715° C.), and (820–885° C.) followed by an exothermic reaction above 870° C. X-ray powder photographs show basal spacings up to the tenth order yielding $d_{001}=17.9$ to 18.0 Å for glycerol treated specimens. The electron micrographs reveal small, irregular thin plates. One sample showed some of the plates curled into tubes. The base-exchange capacity varies from 66 to 128 milliequivalents per 100 grams of sample depending on impurities and chemical composition of the montmorillonite, but independent of particle size. Formulae calculated from the chemical analyses show a fairly wide range of isomorphism. The peak temperatures of the thermal reactions, the "a" and "b" dimensions of the unit cell and base-exchange capacities are correlated with the substitution of magnesium and iron for aluminum in the octahedral layer and aluminum for silicon in the tetrahedral layer as determined from chemical analyses.

Introduction

Many papers have been published on montmorillonite, but practically none of them give convincing evidence that the samples examined were free from impurities. Ross and Hendricks (1) pointed out that they used hand-picked samples checked for impurities with the petrographic microscope. As was noted by them, various kinds of impurities were present in many of the samples which they investigated. They reported that small amounts of impurities are difficult to detect; indeed, as much as one to two per cent of crystalline impurity may escape detection. They also stated that much larger amounts of amorphous silica as well as amorphous hydroxides of aluminum and iron cannot be detected with certainty by microscopic means. They further stated that one sample of montmorillonite was found, by chemical methods, to contain four per cent amorphous silica, and that cristobalite was present in several other samples. As was pointed out by Ross and Hendricks, silica is likely to be the most common impurity in montmorillonite from bentonites.

Kerr, et al (2) showed by microscopic study, x-ray diffraction, thermal analysis, and electron micrography that many of their samples were contaminated with several kinds of mineral impurities. Since impurities of various kinds always affect the interpretation of analytical data, an attempt was made to remove impurities as completely as possible from ten montmorillonites from bentonite. This paper reports the results of a series of studies on at least partially purified montmorillonite from a number of widely distributed localities.

SOURCE OF SAMPLES

All but two of the montmorillonites used in this investigation were from the series of bentonites collected by Kerr, et al (2) as reported to the American Petroleum Institute (*A.P.I. Project 49*). Their report gives a description of the geological occurrence of these samples. Of the two other samples, one was a bentonite from Plymouth, Utah, collected by Dr. D. W. Thorne of the Agricultural Experiment Station, Logan, Utah. His description* of this deposit follows:

> "The bentonite occurs as outcroppings on the foothills along the Northern Utah and Western Idaho border. This sample was obtained about five miles north of Garland, Utah, and about three miles west of a small village called Plymouth on the side of a small ravine. There are large banks of volcanic ash about 100 yards to the west of this outcropping, made up of 90 to 95 per cent volcanic ash and five to ten per cent bentonite. The deposit occurs on top of what is known as Salt Lake Formation. The bentonite was formed through the period of the northwestern lava flow, probably late in Miocene time, by the hydrolysis of volcanic ash which fell into a prehistoric lake."

The other sample was obtained through Dr. H. S. Spence, Consulting Mineral Technologist, Ottawa, Canada. It occurs in a bentonite which outcrops at Quilchena near Merritt, British Columbia, and is described by Spence (3).

METHOD OF PURIFICATION

Hand selected lumps of the crude bentonites approximately air dry were first crushed in a mortar, then leached with 1.0 normal neutral sodium acetate or sodium chloride in order to convert the montmorillonite into the sodium saturated form and thereby bring about ready dispersion of the clay. Leaching with sodium salt solution was continued until a high percentage, but not quite all, of the natural exchangeable bases were replaced by sodium. As far as is known, the clay is affected in no other way by neutral salts. The naturally occurring soluble salts of all kinds, and calcium carbonate if not present in too high percentage, are completely removed by this treatment. The samples were then freed from occluded sodium salt by repeated leaching with 80 per cent neutral methyl alcohol. Distilled water was added, followed by dispersion in a Waring Blendor for ten minutes. Additional distilled water was added, shaken by hand, and the dispersed clay, together with any other remaining substances, was poured into two-liter cylinders and allowed to settle. After standing ten minutes, the suspended clay was siphoned off and allowed to settle overnight. The material remaining in suspension was siphoned off the following day after which the suspensions were passed through a Sharples Super-centrifuge several times. After each centrifugation, the overflow solution was again passed through the centrifuge at a slower rate of throughput and at greater speed of revolution. By this means the sample was separated into a series of particle size fractions. The limit of particle size obtainable by this means is determined by the rate of flow of the suspensions and speed of revolution of the centrifuge. With most of the samples, particles less than 50 mμ, as calculated by Hauser's (4) modification of Stokes' law, were discarded.

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* Private communication to Dr. Paul D. Foote from Dr. D. W. Thorne, June 20, 1949.

By this method each fraction was at first thought to contain particles within a specified range of effective sizes. After the samples had been centrifuged as just outlined, a special study was made on the Santa Rita, New Mexico, bentonite by redispersing each fraction by vigorous shaking in distilled water, then passing the suspension through the centrifuge again. This was repeated ten times. By this means a very high percentage of the clay-like material less than 500 mμ was reduced to particles less than about 50 mμ. In view of these results, the actual range of particle sizes in each fraction discussed in the following pages is open to question. However, the purpose in this part of the work was to secure samples of the montmorillonite as free as possible from impurities. With the exceptions noted later it is believed that this objective was approached fairly closely.

Analytical Results

I. Differential Thermal Analysis.—Differential thermal analysis was carried out using equipment described by McConnell and Earley (6). Since differential thermal analysis is a measure of the energy of reaction as a function of temperature, montmorillonite was compared with inert alumina which was ground to about 200-mesh. The temperatures of the montmorillonite and reference material were measured with platinum/platinum 10% rhodium thermocouples. The samples were heated from about 70° C. to 1000° C. at the rate of 10° C. per minute. The 300–200 mμ fraction of montmorillonite was used for analysis since this fraction is sufficiently coarse to yield distinct reactions and does not contain enough impurities to seriously impair accurate interpretation of the thermograms. The samples were dried at 65° C., allowed to stand in stoppered bottles in contact with air, ground to about 200-mesh and packed in the sample holder using a tamping action (6).

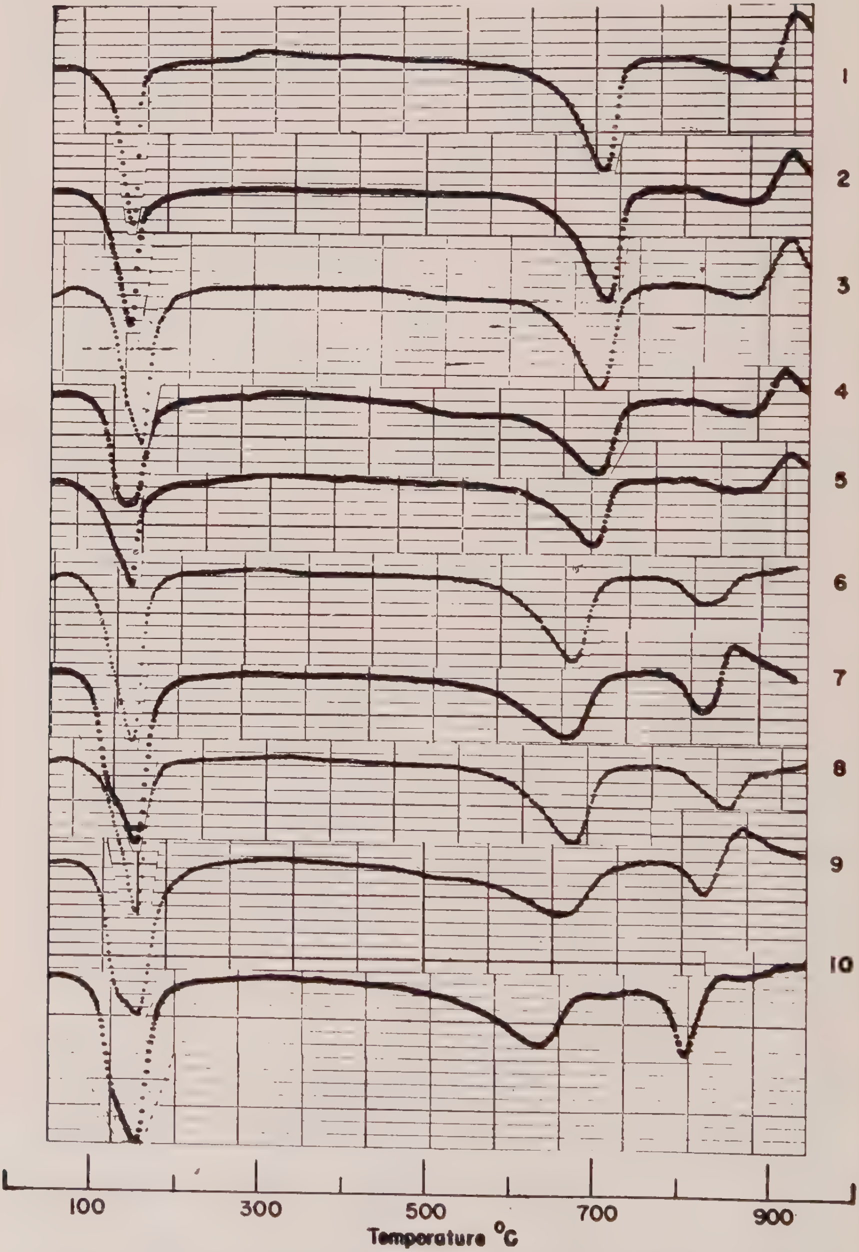
TABLE 1. DIFFERENTIAL THERMAL ANALYSIS DATA

Sample	Peak Temperatures of Thermal Reaction—300–200 mμ Fraction in ° C.						
	Endothermic						Exothermic
Montmorillonite Belle Fourche, South Dakota		140		715		885	930
Montmorillonite Clay Spur, Wyoming		140		715		885	930
Montmorillonite Little Rock, Arkansas		150		710		880	925
Montmorillonite Amory, Mississippi		145	295 545	705		870	910
Montmorillonite Merritt, British Columbia		140		705		875	910
Montmorillonite Polkville, Mississippi		155		690		845	Exo. drift
Montmorillonite Chambers, Arizona		155		685		845	880
Montmorillonite Santa Rita, New Mexico	120	155		680	750	850	Exo. drift
Montmorillonite Plymouth, Utah	135	160	540	675		830	870
Montmorillonite Otay, California		155		650		820	Exo. drift

The differential thermal data shown in Table 1 and Figures 1–10 indicate that sodium-saturated montmorillonite is characterized by three distinct endothermal reactions at 140–160° C., 650–715° C., and 820–890° C. and an exothermal reaction at 880–935° C. or an exothermic drift of the baseline in this temperature range. Assuming the Hofmann-Endell-Wilm (5) structure for montmorillonite, the composite low temperature endotherm is interpreted as due to the removal of one or more sheets of water from the interlayer of the structure and incidental adsorbed water. Since sodium is only slightly hydrated, the water of cation hydration normally given off at about 200° C. is negligible. Some of the samples yield shoulder-type endothermal reactions at 120° C. to 135° C. suggesting that these samples were not dried for sufficient time at 65° C. to remove excess adsorbed water. Thus, the configuration of the low temperature endotherm appears to be markedly affected by the state of hydration of the montmorillonite as pointed out by Hendricks, et al (7). The first high temperature endotherm which occurs at 650–715° C. is attributed to the removal of hydroxyl ions from the octahedral layer. The second high temperature endotherm, 820–890° C., may be accounted for by the release of hydroxyl ions which are held in the tetrahedral layer, or to the breakdown of the montmorillonite structure. The tetrahedral hydroxyl ions, if present, probably occur randomly distributed in the tetrahedral layer substituting for oxygen. It was proposed by Edelman and Favejee (8) that alternate tetrahedral groups have hydroxyl ions, although this explanation would not be compatible with the amount of water determined by Nutting (9) from dehydration experiments. This hypothesis was later modified by the proposal that only occasional tetrahedra have hydroxyl ions. McConnell (10) proposed that the second high temperature endotherm could be accounted for by (H_4O_4) groups in tetrahedral coordination and randomly substituting for (SiO_4) groups. Although any of these explanations might account for the endotherm, none have been proven.

It should be noted that all three endotherms appear to be related. Those samples which yield the low temperature endotherm at the lowest temperature give correspondingly higher temperatures for the high temperature endotherms. This relationship can be accounted for on a basis of chemical composition since substitution of one ion for another results in bond energy changes and by perfection of crystal growth since rates of reaction are partly a function of crystal size. It is obvious in Figs. 1–10 that, as the peak temperature of the first high temperature endotherm decreases, the endotherm tends to become broader, supporting the idea that the rate of water removal is variable . This would not affect the total water but would merely be evidence for isomorphism and variation in the size of crystals.

The exothermic reaction at 870–930° C. is a result of the recombination of the elements in the structure to form oxides. It is doubtful that complete recrystallization takes place in this temperature range. Many of the oxides may remain in an amorphous state until higher temperatures are reached. The exothermic drift shown by some of the samples is probably due to delayed crystallization as suggested by Bradley and Grim (11) or possibly to contraction of the sample from the wall of the sample holder which would result in changes in thermal diffusivity. The temperature at which the exothermal reaction takes place is obviously related to the endothermal reactions suggesting that all of the thermal reactions



FIGS. 1–10. Thermograms of the 300–200 mμ fraction of sodium saturated montmorillonites ground to approximately 200-mesh; thermocouples Pt/Pt 10% Rh; sensitivity ±2.5 microvolts per chart division.

as one would expect are dependent on chemical composition and crystal size. The endotherm at 295° C. for the sample from Amory, Mississippi, suggests the presence of a small amount of finely divided lepidocrocite. The endothermic reaction at 540° C. in the Plymouth, Utah, sample is probably due to a constituent which has not been identified since montmorillonite is not known to have thermal reactions at this temperature.

II. X-Ray Diffraction.—*X*-ray diffraction patterns of montmorillonite samples were obtained by means of a standard Norelco Unit equipped with Debeye-Scherrer type cameras of radius $180/\pi$mm. The patterns were all produced with FeKα radiation.

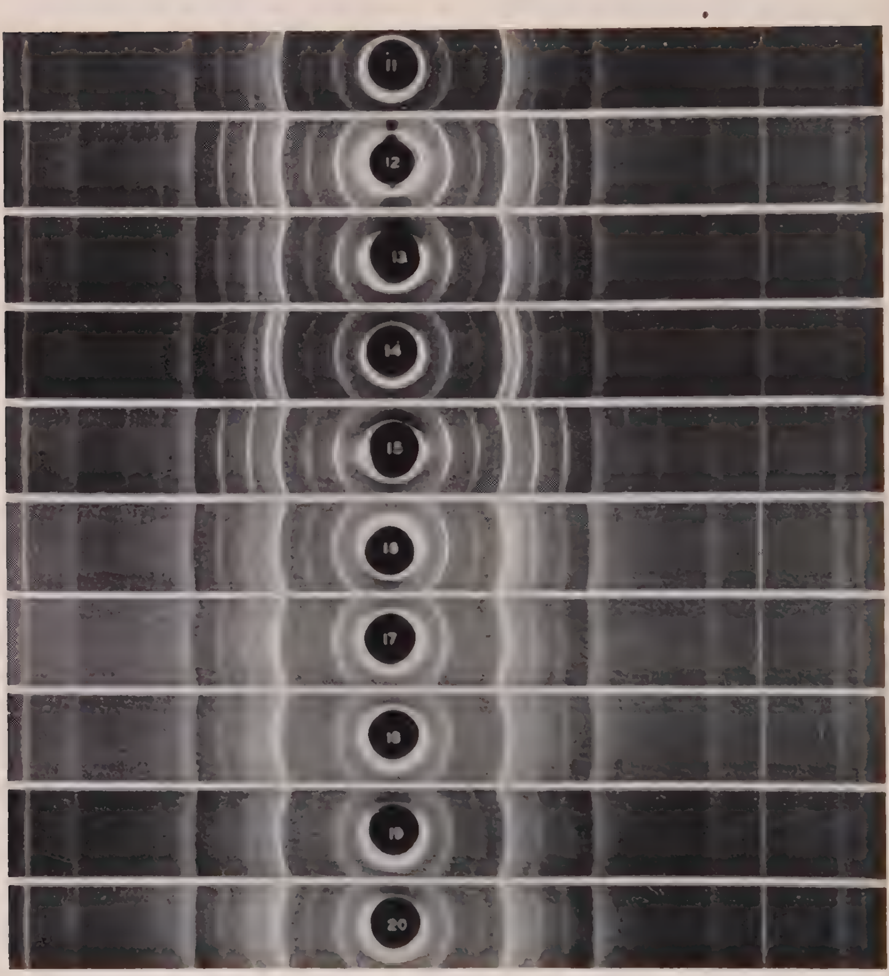
Powder samples were prepared from the 200–70 mμ fraction of the sodium saturated montmorillonites which had been dried at 65° C. The samples were thoroughly mixed with glycerol and evaporated at 125° C. until the residue became thick and almost dry. At this point, sufficient glycerol remains to enable one to roll a specimen into a rod which can be mounted in the powder camera directly without the aid of any supporting material. All specimens were prepared in this manner and rolled into rods approximately 0.25 mm. in diameter. All photographs were taken in the same powder camera and exposed for 20 hours.

The powder patterns which are reproduced in Figures 11–20 inclusive all show a very strong diffraction line with $d(001)=17.5$ to 17.9 Å. Higher orders of the basal spacing to (00.10) are present in some of the photographs. Calculation from $(00l)$ measurements yields $d(001)=17.9$ to 18.0 Å. *X*-ray diffraction data for each of the samples are presented in Table 2.

Impurities are still evident in several of the samples. Cristobalite is present in large quantities in the Merritt, British Columbia, sample and in a somewhat lesser amount in the Santa Rita, New Mexico, material. It can be also detected in samples from Belle Fourche, South Dakota, and Little Rock, Arkansas, on the basis of the strongest line. The presence of a diffraction line at 3.30 Å suggests hydrous mica in the Amory, Mississippi, sample. This observation is consistent with the presence of about 0.60 per cent non-exchangeable K_2O in this material. Except in the case of the cristobalite in the Santa Rita, New Mexico, and Merritt, British Columbia clays, these impurities probably do not constitute more than 5 per cent of the samples.

In addition to the $(00l)$ diffraction lines, the patterns all show $(hk0)$

FIG. 1. Belle Fourche, South Dakota.
FIG. 2. Clay Spur, Wyoming.
FIG. 3. Little Rock, Arkansas.
FIG. 4. Amory, Mississippi.
FIG. 5. Merritt, British Columbia.
FIG. 6. Polkville, Mississippi.
FIG. 7. Chambers, Arizona.
FIG. 8. Santa Rita, New Mexico.
FIG. 9. Plymouth, Utah.
FIG. 10. Otay, California.



FIGS. 11–20. X ray powder photographs with FeKα radiation of the 200–70 mμ fractions of sodium-saturated, glycerol-treated montmorillonites; camera radius 180/πmm.

FIG. 11. Santa Rita, New Mexico.	FIG. 16. Polkville, Mississippi.
FIG. 12. Belle Fourche, South Dakota.	FIG. 17. Amory, Mississippi.
FIG. 13. Little Rock, Arkansas.	FIG. 18. Chambers, Arizona.
FIG. 14. Merritt, British Columbia.	FIG. 19. Plymouth, Utah.
FIG. 15. Clay Spur, Wyoming.	FIG. 20. Otay, California.

lines which apparently do not differ in measurement beyond the expected experimental error. However, a separate careful measurement of the (330) (060) line on each of the films has shown that individual measurments can be reproduced within 0.001 Å and that there are appreciable differences in the spacing of (330) (060) between the various montmoril-

TABLE 2. MONTMORILLONITES *X*-RAY POWDER DIFFRACTION DATA
200–70 mμ Fractions, Na-Saturated, Glycerol Saturated

Santa Rita, N. Mex.		Belle Fourche, S. Dak.		Little Rock, Ark.		Merritt, B.C.		Clay Spur, Wyo.		Polkville, Miss.		Amory, Miss.		Chambers, Ariz.		Plymouth, Utah		Otay, Calif.		
I	*dA*	*I*	*dA*	*I*	*dA*	*I*	*dA*	*I*	*dA*	*I*	*dA*	*I*	*dA*	*I*	*dA*	*I*	*dA*	*I*	*dA*	Interpretation
10	17.5	10*b*	17.6	10	17.8	10	17.6	10	17.9	10*b*	17.6	10*b*	17.7	10	17.6	10	17.6	10*b*	17.7	(001)
6	9.00	7	9.04	6	8.98	6	9.01	7	9.03	5	8.97	5	9.01	5	9.00	5	9.04	5	9.04	(002)
4	5.98	4	5.98	2	5.98	3	5.99	4	6.02	3	5.93	1	5.96	1	5.99	2	5.95	2	5.95	(003)
1	4.97	1	4.94	1	4.95	1	4.94	1	4.98	1	4.93	1	4.98	1	4.95	1	4.97	½	4.93	β (110) (020)
9	4.48	8	4.49	7	4.51	7	4.50	8	4.51	8	4.48	8	4.50	8	4.49	8	4.50	8	4.48	(110) (020)
5	4.08	½	4.13	½	4.13	8	4.07													α Cristobalite
		½	3.96					½	3.95	1*b*	3.95	1*b*	3.94	1*b*	3.91					β(005)
6	3.58	6	3.58	5	3.58	5	3.58	7	3.60	4	3.58	4	3.57	4	3.58	5	3.58	4	3.58	(005)
												1	3.30							Hydrous Mica
						1	3.14													α Cristobalite
5	2.99	5	2.99	4	2.99	4	3.00	5	3.01	3	2.98	3	3.00	3	2.99	3	2.99	3	2.99	(006)
						1	2.85													α Cristobalite
5*b*	2.58	4*b*	2.58	4*b*	2.59	4*b*	2.57	4*b*	2.59	4*b*	2.58	5*b*	2.58	4*b*	2.57	5*b*	2.58	5*b*	2.58	(130) (200)
						5	2.487													α Cristobalite
3	2.242	3	2.246	1	2.246	1	2.248	3	2.250	2	2.242	1	2.250	1	2.242	2	2.246	2	2.244	(220) (040)
						½	2.126													α Cristobalite
						½	2.038													α Cristobalite
1	1.993	2	1.995	1	1.989	½	1.989	3	2.001	1	1.993	½	1.981	½	1.989	½	1.976	½	1.989	(009)
						½	1.936													α Cristobalite
						½	1.878													α Cristobalite
½	1.793	1	1.794			½	1.799	½	1.803											(00.10)
5	1.700	3	1.703	3	1.706	2	1.699	3	1.701	2	1.705	2	1.702	2	1.699	2	1.704	4	1.705	(240) (310)
½	1.658	1	1.658	½	1.660	½	1.660			½	1.655	½	1.662			½	1.656	½	1.656	β (330) (060)
7	1.501	5	1.501	5	1.502	6	1.501	6	1.503	6	1.504	6	1.505	6	1.504	6	1.504	7	1.504	(330) (060)
2*b*	1.296	2*b*	1.299	2	1.297	2*b*	1.298	2*b*	1.300	1*b*	1.298	1*b*	1.299	1*b*	1.294	1*b*	1.298	2*b*	1.299	(260) (400)
2	1.250	2	1.248	3	1.251	2	1.250	2	1.254	1	1.251	1	1.252	1	1.250	1	1.252	2	1.250	(250) (170) (420)

b = broad line.

lonites. The spacings for this line, which are given in Table 2, are those obtained by this separate measurement on the film. In order to further improve the accuracy of these measurements, specimens were examined with a Philips high angle Spectrometer (CuKα radiation). The values obtained in this manner for the spacing of (330) (060) are as follows:

	2θ(330)(060)	d(330)(060)
Montmorillonite, Santa Rita, New Mexico	61.90	1.4989 Å
Montmorillonite, Belle Fourche, South Dakota	61.90	1.4989
Montmorillonite, Little Rock, Arkansas	61.88	1.4993
Montmorillonite, Merritt, British Columbia	61.85	1.5000
Montmorillonite, Clay Spur, Wyoming	61.84	1.5002
Montmorillonite, Polkville, Mississippi	61.83	1.5004
Montmorillonite, Amory, Mississippi	61.82	1.5007
Montmorillonite, Chambers, Arizona	61.82	1.5007
Montmorillonite, Plymouth, Utah	61.77	1.5018
Montmorillonite, Otay, California	61.74	1.5024

It is considered that the 2θ measurements from the spectrometer traces are reproducible to ±0.01° and consequently the d values are subject to a variation of ±0.0002 Å.

III. Electron Microscopy.—Samples of the 200–70 mμ fraction of the ten montmorillonites were examined with the electron microscope. In all of the samples the clay particles appear as irregular flakes and masses. Montmorillonite from Clay Spur, Wyoming, shows well defined thin flakes in various stages of curling into tubes (Fig. 21) similar to the observations of Ardenne, et al (12) but which they interpret as crystals standing on edge. The appearance of the flakes suggests that the curling may be due to the process of drying during preparation of the sample or to the heating effect of the electron beam, rather than to an inherent structure. As a result of this curling, many flakes show straight edges, thus giving a false impression of crystal outline. Minor evidence of curling was seen in the electron micrograph of the Belle Fourche montmorillonite.

Curling, or development of tubes, has been observed with the mineral halloysite (13) and has been explained as the result of an imperfect fit in this two layer structure between the silicon-oxygen sheet and the hydroxyl sheet of the octahedral layer. A structural unit of the hydroxyl sheet normally has a smaller spacing than an equivalent unit of the silicon-oxygen sheet. With a water layer between two layer units, it seems possible that the next silicon-oxygen layer is unable to exert enough "stretching" force on the hydroxyl sheet to prevent a curling effect, which results in the development of tubes.

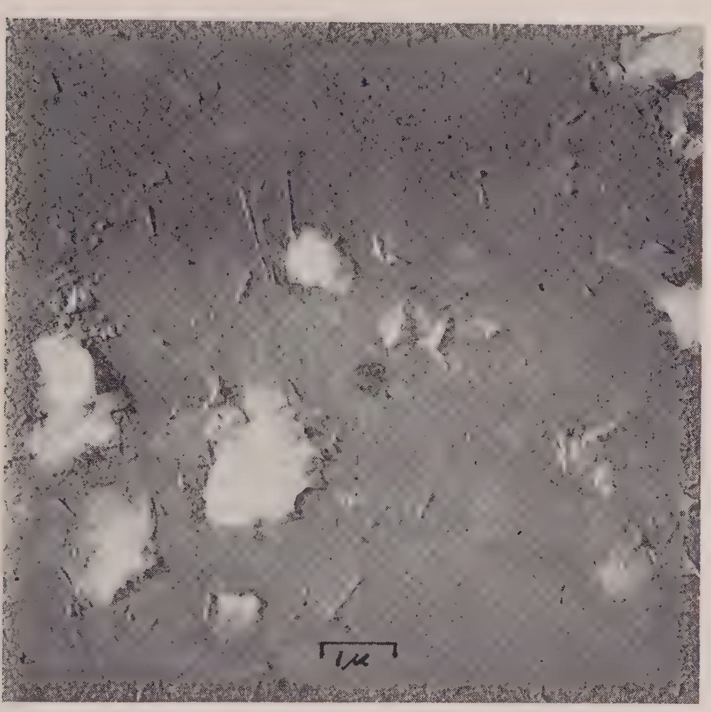


FIG. 21. Electron micrograph of the 200–70 mμ fraction of sodium saturated montmorillonite, Clay Spur, Wyoming, prepared from a water suspension which was evaporated onto a Formvar film supported on a standard screen, Pd—shadowed.

This explanation cannot be applied to montmorillonite since, in accordance with the Hofmann-Endell-Wilm structure, it has silicon-oxygen layers on both sides of an octahedral layer. Furthermore, there is not a continuous hydroxyl layer present. In this three layer structure, substitution in the tetrahedral or octahedral layers gives rise to equal forces on both sides of the "sandwich" and cannot produce curling. The curling which has been observed has always been in an upward direction and appears, therefore, to be due to drying effects during preparation and observation of the sample.

A more likely explanation involves the physical nature of the observed flakes and the actual size of clay crystals. It has already been suggested that the particle size attributed to the various clay fractions separated by centrifugation is that of aggregates rather than individual crystals. It has been concluded, therefore, that the curled flakes observed in the electron micrographs are aggregates formed during the preparation of the sample from a thin suspension. Since the crystals are presumably platy in nature, the aggregates will be composed of many overlapping flakes along with entrapped water. Dehydration during evacuation of the electron microscope and by the heating effects of the electron beam, removes water from the upper portion of the aggregates most easily. This removal of water (not interlayer water) and the accompanying surface tension effects will draw the edges of flakes closer together, thereby causing the aggregate to curl upward. This phenomenon will be most apparent when the crystals occur as unusually large plates which should increase the differential drying effects between the top and bottom of the aggregates. It has been noted that those montmorillonites which show preferred orientation effects most readily in *x*-ray diffraction specimens and have the sharpest diffraction lines are the ones which exhibit the curling effect. This, in turn, suggests that crystal size and shape vary considerably in montmorillonites.

IV. Base-Exchange Capacity and Chemical Analysis.—The base-exchange capacities of these montmorillonites, both in their natural state and in various particle size fractions after sodium saturation have been reported by Osthaus (14). The data show a wide variation of the exchangeable cations present in the untreated montmorillonites. The base-exchange capacities of five particle size fractions of the purified sodium saturated montmorillonites show in some cases fairly constant values, while in others the base-exchange capacity increases markedly in the fractions less than 300 mμ. This increase in base-exchange capacity in the fine fractions is very likely due to concentration of impurities in the coarse fractions as suggested by Osthaus. However, the purity of a fine fraction cannot be inferred from the fact that the base-exchange capacity remains constant over a range of fine particle sizes. This is illustrated by the Merritt, British Columbia, and Santa Rita, New Mexico, samples which show a constancy of base-exchange capacity over the three finest particle size fractions but still contain large amounts of cristobalite.

Osthaus has suggested, on the basis of his data from specimens which appear to be relatively pure, that base-exchange capacity is independent of the particle size as calculated by Hauser's modification of Stoke's law. This could mean, of course, that the indicated particle size even in the finest fraction is that of aggregates of crystals, rather than individual crystals.

Chemical analyses and calculated structural formulae have been reported by Osthaus (14) for eight of the ten montmorillonites included in this paper. Additional analyses for montmorillonite from Little Rock, Arkansas, and from Amory, Mississippi, along with those already reported are given in Table 3. As outlined by Osthaus, a determination of soluble silica and alumina was made for each sample by means of an extraction with 0.5 normal sodium hydroxide.

TABLE 3. CHEMICAL ANALYSES AND BASE EXCHANGE CAPACITY OF MONTMORILLONITE (200–70 mμ) After Sodium Saturation

	Belle Fourche, South Dakota	Clay Spur, Wyoming	Little Rock, Arkansas	Plymouth, Utah	Merritt, Br. Col.	Amory, Mississippi	Chambers, Arizona	Santa Rita, New Mexico	Polkville, Mississippi	Otay, California
SiO_2	61.12	61.47	60.69	58.60	71.60	59.30	61.16	65.21	63.42	63.04
Al_2O_3	23.10	22.17	22.40	20.64	15.75	20.40	20.38	19.13	19.44	18.44
Fe_2O_3	4.37	4.32	5.67	4.89	3.78	7.74	3.66	1.07	1.87	1.20
TiO_2	0.09	0.09	0.19	0.57	0.24	0.76	0.37	0.14	0.32	0.14
MnO	trace	trace	0.00	0.03	trace	0.07	0.03	0.03	0.00	0.01
P_2O_5	0.05	0.02	trace	0.02	0.04	0.14	0.03	trace	0.04	0.05
CaO	0.24	0.14	0.00	0.64	0.07	0.03	0.14	0.04	0.11	0.08
MgO	2.50	2.73	1.87	4.00	0.97	2.40	4.52	4.57	5.00	7.30
Na_2O	2.90	3.18	2.50	3.00	1.88	2.52	3.70	3.90	3.46	3.40
K_2O	0.04	0.03	0.13	0.07	0.09	0.66	0.04	0.14	0.08	0.02
H_2O	5.84	6.02	6.61	7.63	5.34	6.25	6.40	5.83	6.15	6.47
Total	100.25	100.17	100.06	100.09	99.76	100.27	100.43	100.06	99.89	100.15
Sol.* SiO_2	6.74	3.59	7.88	8.00	29.90†	6.59	5.80	8.00	8.40	3.92
Sol.* Al_2O_3	1.50	0.64	2.25	2.08	0.68	1.58	1.71	0.86	2.25	1.02
B.E.C.‡	94.2	103.0	86.8	118.4	65.9	84.7	124.0	117.0	121.0	128.3

* Determined by sodium hydroxide extraction.

† Determination of uncombined silica by phosphoric acid method of Talvitie (16) gave 37.65%.

‡ Base-exchange capacity in milliequivalents per 100 grams of clay dried at 85° C.

NOTE: Data for montmorillonites from Belle Fourche, South Dakota; Clay Spur, Wyoming; Plymouth, Utah; Merritt, British Columbia; Chambers, Arizona; Santa Rita, New Mexico; Polkville, Mississippi; and Otay, California from Osthaus (14).

TABLE 4. DISTRIBUTION OF CHARGES ON LATTICE LAYERS AND STRUCTURAL FORMULAE OF TEN SODIUM SATURATED MONTMORILLONITES AFTER DEDUCTING SOLUBLE SiO_2 AND Al_2O_3; 200–70 mμ FRACTION

		Belle Fourche, S. Dak.	Clay Spur, Wyo.	Little Rock, Ark.	Ply-mouth, Utah	Merritt, Br. Col.	Amory, Miss.	Chambers, Ariz.	Santa Rita, N. Mex.	Polk-ville, Miss.	Otay, Calif.
Tetrahedral	Si	7.539	7.671	7.597	7.465	7.308	7.552	7.692	7.930	7.886	7.899
	Al	0.461	0.329	0.403	0.535	0.692	0.448	0.308	0.070	0.117	0.101
	Total	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
	Charge	−0.461	−0.329	−0.403	−0.535	−0.692	−0.448	−0.308	−0.070	−0.114	−0.101
Octahedral	Al	3.068	3.033	3.013	2.692	3.131	2.729	2.748	2.912	2.789	2.642
	Fe	0.456	0.431	0.613	0.543	0.612	0.834	0.383	0.112	0.202	0.121
	Mg	0.516	0.539	0.401	0.864	0.311	0.512	0.929	0.943	1.067	1.419
	Total	4.040	4.003	4.027	4.099	4.054	4.075	4 060	3.967	4.058	4.182
	Charge	−0.396	−0.530	−0.320	−0.567	−0.149	−0.287	−0.749	−1.042	−0.893	−0.873
Layer Charge		−0.857	−0.859	−0.723	−1.102	−0.841	−0.735	−1.057	−1.112	−1.007	−0.974
Interlayer	Na	0.777	0.816	0.696	0.858	0.784	0.699	0.996	1.048	0.961	0.880
	K	0.007	0.005	0.024	0.013	0.024	0.023	0.007	0.025	0.014	0.003
	Ca	0.035	0.020	—	0.101	0.016	0.009	0.020	0.006	0.017	0.011
	Mg	—	—	—	0.015	—	—	0.007	0.014	—	0.034
Interlayer Charge		+0.854	+0.861	+0.720	+1.103	+0.840	+0.740	+1.057	+1.113	+1.009	+0.973

NOTE: Data for montmorillonites from Belle Fourche, South Dakota; Clay Spur, Wyoming; Plymouth, Utah; Merritt, British Columbia; Chambers, Arizona; Santa Rita, New Mexico; Polkville, Mississippi; and Otay, California from Osthaus (14).

The calculated structural formulae showing the distribution of lattice charges for the eight analyses reported by Osthaus and those for the Amory and Little Rock materials are given in Table 4. The analyses have been calculated according to the method of Kelley (15) after correcting for soluble silica and alumina. Osthaus has pointed out the uncertainty that the silica and alumina removed by sodium hydroxide are impurity or partial solution of the silicate. There is little doubt that the purity of the Santa Rita and Merritt samples is enhanced by this treatment since *x*-ray examination of the treated products shows no evidence of crystalline silica. On the other hand, samples which did not show crystalline impurities yielded appreciable silica and alumina upon extraction suggesting that these materials were admixed in an amorphous state or that some of the montmorillonite was dissolved. No attempt has been made to correct for iron that may be extraneous to the clay lattice although it seems likely that this element is present as an oxide or hydrate in the samples which contain five or more per cent Fe_2O_3.

Discussion and Conclusions

A necessary aim of a study of this kind is the correlation of the various sets of analytical data within our concepts of the crystal structure and properties of montmorillonite. The basis of such correlation must be chemical analysis but, unfortunately, this method of investigation is sensitive to errors because of impurities. Five of the ten purified samples which have been studied give *x*-ray diffraction evidence of crystalline impurities and it is considered that the remainder may contain more or less amorphous silica and alumina. Although attempts have been made to remove free silica and alumina by sodium hydroxide extractions, it is not certain that this method is completely reliable. No attempt has been made to remove hydrous mica from the Amory sample. Therefore, the chemical analyses and structural formulae can be accepted only as close approximations. Nevertheless, the structural formulae suggests a fairly wide range of isomorphism. The same criticism may be made of the base-exchange determinations which must be decreased by the presence of impurities which do not possess base-exchange properties. The *x*-ray and differential thermal analysis data are probably not altered greatly by small amounts of impurities. However, the temperatures of thermal reactions of layer silicates containing hydroxyl groups are decreased by decreasing particle size as indicated by the experimental results of Kelley, et al. (17) and Kulp and Trites (18). The thermal reactions must be controlled primarily by chemical composition but modified by particle size. It has already been suggested from electron micrographic evidence that particle size varies considerably in this group of montmorillonites.

In Table 5 the spacing values of (330) (060) are given as measured by the *x*-ray spectrometer. These values are compared with the ratio of octahedral iron plus magnesium to total octahedral cations and it will be seen that, in general, increasing iron plus magnesium content is accompanied by an increase in the spacing of (330) (060). This is to be expected since the iron and magnesium atoms are larger than the aluminum atom. The relationship is not precise, particularly in the samples with a small ratio, but since some of these samples contained cristobalite it is likely that the ratio is somewhat unreliable. An additional factor, the isomorphous substitution of aluminum for silicon in the tetrahedral layer, which has not been taken into account in this comparison may have some effect on lattice dimensions. The temperatures of the first high temperature endotherm have been included in this table as well as the base-exchange values corrected for the removal of soluble silica and alumina. It will be seen that these two properties show some correlation, high base-exchange values being accompanied by low endotherm temperatures. From the ratios shown in Table 5 it is suggested that the substitution of iron and magnesium for aluminum in the octahedral layer of montmorillonite reduces the peak temperature of the first high temperature endotherm. There are important exceptions in the case of the Santa Rita and Amory samples which have lower and higher tempera-

TABLE 5. COMPARISON OF PHYSICAL AND CHEMICAL PROPERTIES OF MONTMORILLONITES

Locality	$\frac{\text{Octahedral Fe+Mg}}{\text{Total Octahedral Cations}}$	d(330)(060)	Peak Temp. First High Temp. Endotherm	Base-Exchange Capacity*
Santa Rita, New Mexico	0.266	1.4989 Å	680° C.	128.4
Belle Fourche, South Dakota	0.240	1.4989	715° C.	102.7
Little Rock, Arkansas	0.252	1.4993	710° C.	96.6
Merritt, British Columbia	0.228	1.5000	705° C.	106.9
Clay Spur, Wyoming	0.243	1.5002	715° C.	107.5
Polkville, Mississippi	0.313	1.5004	690° C.	136.3
Amory, Mississippi	0.331	1.5007	705° C.	92.2
Chambers, Arizona	0.325	1.5007	685° C.	134.1
Plymouth, Utah	0.343	1.5018	675° C.	131.7
Otay, California	0.368	1.5024	650° C.	135.0

* Milliequivalents per 100 grams; corrected for subtraction of soluble SiO_2 and Al_2O_3.

tures respectively than would be expected from the apparent trend of the table. These exceptions indicate that an additional factor or factors other than chemical composition must be considered in interpreting these thermal reactions. It is suggested by the authors that the particle size of crystals may account for these anomalies. This would imply that the crystal size of the Santa Rita sample is small compared with the Belle Fourche sample which has almost the same octahedral ratio; in the case of the Amory montmorillonite, the higher temperature of its thermal reactions would indicate a crystal size larger than that of its neighbors in the table with similar octahedral ratios. In both of these cases, the base-exchange capacity also does not conform with the apparent trend of the table, that of the Santa Rita material being high while that of the Amory sample is low. These base-exchange capacities are adequately explained by isomorphous substitution, but some speculation on the apparent relationship between base-exchange capacity and thermal reaction temperatures appears to be justified. The obvious inference, in view of the arguments above, is that crystal size is directly related to base-exchange capacity. By this it is meant that the base-exchange capacity of montmorillonite may be indicative of structural factors which limit the maximum size of crystals and that a large base-exchange capacity is accompanied by small crystal size.

This study has indicated the need for improved methods of purification of montmorillonites in order to obtain accurate chemical data on this group of minerals. Improved purity and a more detailed knowledge of the shape and size of crystals will probably provide the answer to many of the anomalies which exist in analytical data.

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Dr. W. P. Kelley, Professor Emeritus of the University of California and Mr. Ben B. Cox, Director of the Geology Division of the Gulf Research and Development Company, gave generously of their time supervising this study and assisting in the preparation of this report. The assistance rendered by other members of the Gulf Research and Development Company is greatly appreciated, particularly the preparation of the electron micrographs by Dr. R. T. Koenig of the Physics Division.

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NOTES AND NEWS

ON THE DISTINCTION OF SILLIMANITE FROM MULLITE BY INFRA-RED TECHNIQUES

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The problem of distinguishing mullite from sillimanite has attracted the attention of several mineralogists. The extensive similarity in *x*-ray diffraction patterns and optical properties of sillimanite and mullite has been recognized ever since the original correction was made on the alumina-silica system by Bowen and Greig (1924). Recent attempts to distinguish between these phases has been largely dependent on *x*-ray methods (de Keyser, 1951, McAttee and Milligan, 1950). The optical properties of the material also may be used to distinguish between the two phases although some authors claim an overlap in these. A positive method available at the present time is through a study of the thermal properties of the material, since liquid appears in the sillimanite composition at 1585° as compared with 1810° C. for the mullite composition. None of these methods, however, is applicable where the material is very fine-grained and mixed with other phases. During studies of phase equilibria in the systems Al_2O_3-SiO_2-H_2O (1951) and MgO-Al_2O_3-SiO_2-H_2O (1951), Roy, Roy and Osborn were unsuccessful in positively identifying any of the phases formed as being sillimanite, andalusite or kyanite. Recently andalusite has been reproducibly synthesized (Roy, 1953), stimulating interest in the identification of the phase which had been earlier identified as mullite in the absence of any positive evidence for sillimanite.

During the last two years papers describing the use of infra-red absorption spectra of mineral powders have been numerous and in two of these (Adler, 1950, Keller, 1952) spectra may be found for sillimanite and mullite. Although only single specimens were used, these spectra are different from each other, as noted by Adler (1950). We have therefore investigated this technique further as a possible rapid qualitative method of distinguishing sillimanite from mullite. If the differences are pronounced, it would also indicate the possible usefulness of infra-red techniques in distinguishing phases differing only slightly in structure.

A Perkin Elmer Model 12A instrument with a NaCl prism was used in this investigation. Sillimanite samples were chosen from various localities and mullite was also obtained by various methods as listed in Table 1. All the samples were checked optically and by *x*-ray powder patterns. The effect of both particle size and methods of preparation were taken

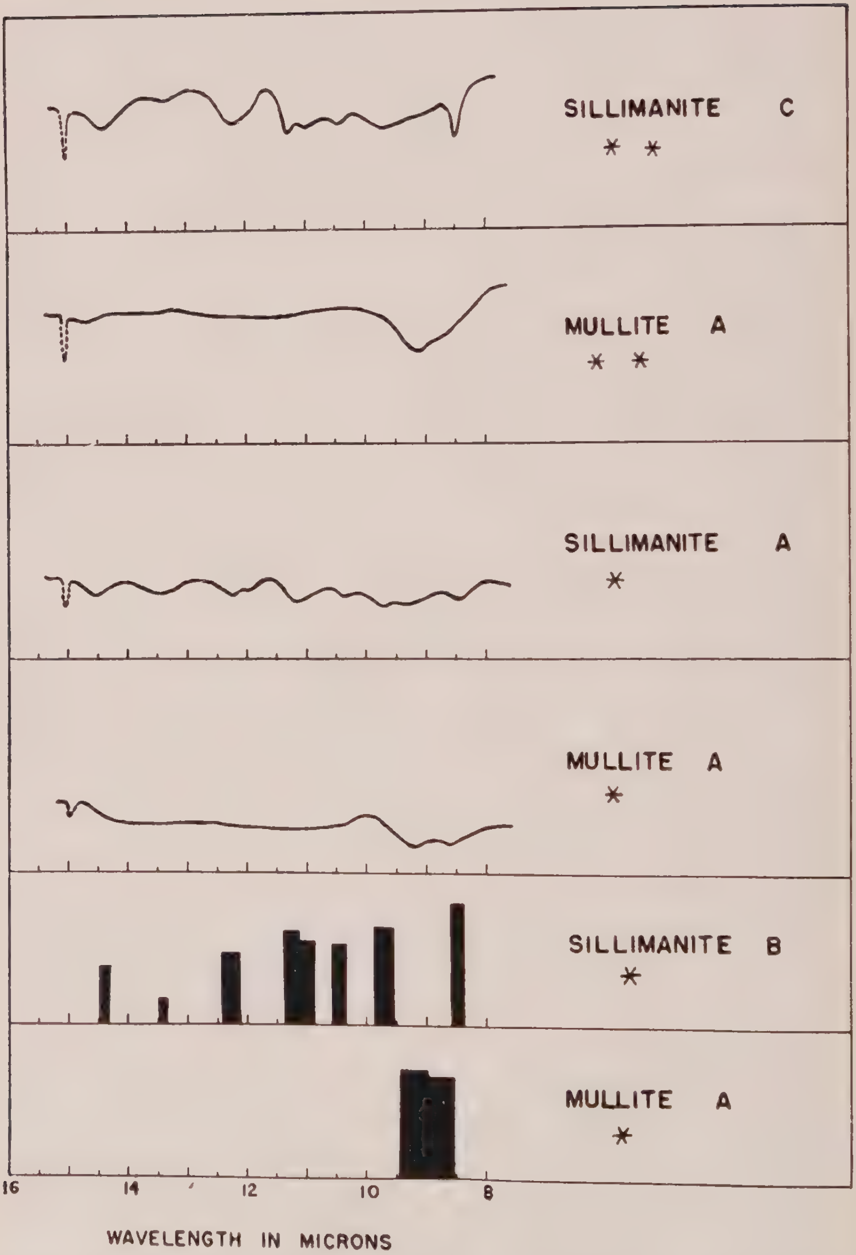

Fig. 1. Typical infra-red absorption curves for sillimanite and mullite. Relative transmission is plotted on the vertical axis. Curves with a single star were obtained with a suspension in Nujol; those with two stars were obtained from samples evaporated from ethyl alcohol, film density .3 mgm./sq. cm. The block diagrams are of the type shown by Launer (1952).

TABLE 1

Sillimanite	A	U. S. National Museum Specimen No. 3732, Brandywine Springs, Del.
	B	U. S. National Museum Specimen No. 3731, Norwich, Conn.
	C	Genth Collection (School of Mineral Industries, The Penna. State College) No. 399.13, Unionville, Pa.
Mullite	A	Single crystals of electrically fused mullite (Corhart).
	B	Langley kaolinite heated to 1350° C. for 12 hours showing essentially complete conversion to mullite and cristobalite.

into consideration. Relatively coarse particles (−325 mesh) and various size fractions calculated to be less than 2μ, and less than $\frac{1}{4}\mu$ were obtained by sedimentation in absolute alcohol. The samples were either mulled in Nujol and applied to the NaCl plates, or applied as a suspension in absolute alcohol and the alcohol evaporated. The film density varied from 0.1 mgm. to 1 mgm. per sq. cm. in thickness (see Launer, 1952). The mullite samples always gave essentially the same pattern and the sillimanite samples likewise gave the same pattern under all conditions and the patterns of the minerals are quite distinct. Block diagrams such as those recently used effectively by Launer (1952) while not as precise as percentage transmission curves are considerably more useful for such crude identification procedures. Diagrams are shown for the spectra of sillimanite and mullite. It will be seen that mullite has a pronounced absorption at 9.1μ and minor absorption maxima near 8.6μ; whereas sillimanite has several absorption maxima at 8.45, 9.7, 10.45, 11.0, 11.3, 12.25, 13.4 and 14.4μ. A low sharp absorption at 6.20μ is not shown since it may not be unique for sillimanite for it did not appear in the coarser samples and may be an impurity in the very fine fractions. It is evident therefore that sillimanite may be distinguished from mullite by very simple experimental techniques. A −325 mesh powder (finer grinding helps greatly) mulled in Nujol is sufficient to provide a distinctive infra-red absorption pattern in the 8–15μ range.

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AUGELITE FROM PEGMATITES IN NEW HAMPSHIRE

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Augelite, $Al_2(PO_4)(OH)_3$, has been found in granite pegmatite at two localities in New Hampshire: the Smith mine at Chandler's Mill near Newport, and the Palermo mine near North Groton. The Smith mine was worked for mica during the summer of 1952. Specimens were obtained from the dump heap showing transparent, pale aquamarine-blue crystals associated with lazulite, albite and quartz. The blue crystals were identified as augelite from their optical properties: biaxial positive, 2V medium, with $\alpha=1.574$, $\beta=1.576$ and $\gamma=1.588$. The identification was confirmed by an *x*-ray powder photograph. The crystals are embedded and poorly formed. Tiny blue inclusions can be seen under low magnification, and the color of the mineral apparently is due to disseminated particles of lazulite. Augelite crystals from the locality at Laws, California, show a similar feature. The Smith pegmatite shows a marked lithium and phosphate phase. Triphylite, lazulite and granular apatite are the most common phosphate minerals. The lazulite occurs in a heterogeneous manner throughout the pegmatite in small masses, and the augelite occurs immediately associated with it. Other less common phosphates that occur at the locality include hurlbutite, tiny beryllonite crystals, small twinned crystals of amblygonite and brazilianite as small single crystals and as aggregates of parallely intergrown crystals up to an inch in length.

Augelite also occurs in the well known Palermo pegmatite near North Groton. The mineral was first identified by A. L. Mackay of the University of London, who found crystals on specimens of whitlockite that had been sent to him for study. A number of additional specimens were then recognized in bulk lots of Palermo material carrying whitlockite and brazilianite that had been collected in 1947 and 1948 and placed in storage pending further study. The mineral occurs both as anhedral colorless masses up to 1 cm. in size embedded in a granular matrix of quartz, siderite and feldspar, and as small crystals associated with whitlockite, brazilianite, goyazite, quartz, siderite and apatite in drusy cavities. The granular matrix occasionally contains disseminated grains of dark blue lazulite. The augelite crystals, although monoclinic, usually have a markedly pseudo-rhombohedral habit, very similar to that figured by Prior and Spencer[1] for augelite from Bolivia. Such crystals are virtually indistinguishable on casual examination from whitlockite crystals that have the common $\{01\bar{1}2\}$ habit. The augelite crystals often have a white, frosted surface due to slight etching, but others are colorless and glassy. Optically, the crystals have α 1.573, β 1.576 and γ 1.587, with 2V medium.

A PROPOSED PETROGRAPHIC METHOD FOR THE RAPID DETERMINATION OF ILMENITE

Roberts M. Wallace, *University of Arizona, Tucson, Arizona.*

Recently, while studying crushed fragments of opaque minerals under the petrographic microscope, it was noticed that many ilmenite fragments could be easily distinguished from all other opaque fragments by a distinct orange-red color appearing on the very thin edges of the fragments. This effect was noticed only under crossed nicols and with the upper lens of the condenser swung into position. A rather strong source of light is necessary which the condenser aids in illuminating the thin edges of the fragments.

The fragments of the opaque minerals were mounted on slides with a few drops of Canada Balsam or immersed in oil ($n = 1.545$) and then covered with a thin cover glass. The effect was seen in fragments from 1/4 mm. to less than 1/16 mm. sizes (50 to 150 mesh A.S.T.M. or Tyler Standard Screen Scale sieves 264 to 62). In the smaller sizes, minute particles often exhibit orange-red translucency throughout the grains.

Observations of ilmenite specimens from Norway, Maryland, California, Arizona, and three of unknown locality showed this distinct color effect on the thin edges. To date the writer has not found any other opaque mineral, that, when crushed, will give this distinct orange-red color. The closest mineral resemblance found under these conditions was that of specular hematite. However ilmenite can be readily distinguished from specular hematite as the latter has a more blood-red color which is visible also without the aid of the condenser lens. The color in specular hematite may also be seen in plane light. It was noticed that magnetite appeared as a light grayish yellow in a few of the thinnest edges while viewed under the same conditions as in observing the ilmenite fragments. Likewise picotite appeared a light tan color on thin edges.

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[1] Prior, G. T., and Spencer, L. J.: *Mineral. Mag.*, **11**, 16 (1895).

The explanation of this phenomenon in an opaque mineral is not known to the writer, but the observations, and the conditions under which they were made, are recorded here in the hope that they will be of use to students working with opaque detrital grains. These would probably need to be crushed to obtain angular fragments. The author will be glad to learn whether others obtain the same result with crushed grains of ilmenite.

HOPPER CRYSTALS OF HALITE IN THE SALINA OF MICHIGAN

L. F. Dellwig, *University of Michigan, Ann Arbor, Michigan.*

In the manufacture of grainer salt, crystal growth is effected by evaporation at temperatures below boiling in order to prevent turbulence and permit the formation of a thin surface film of high density brine. In this film the halite crystals begin to grow. As growth continues the cube tends to sink under its own weight although it is held at the surface by surface tension. Because only one cube face of the crystal is in contact with the high density film, growth takes place only along its edges. In this manner, while the crystal sinks, growth continues upward and outward along these edges resulting in a hollow pyramid with its apex pointing downward. When the surface is disturbed the crystals are broken or swamped and sink. Manufactured crystals of this sort are shown in Figure 1.

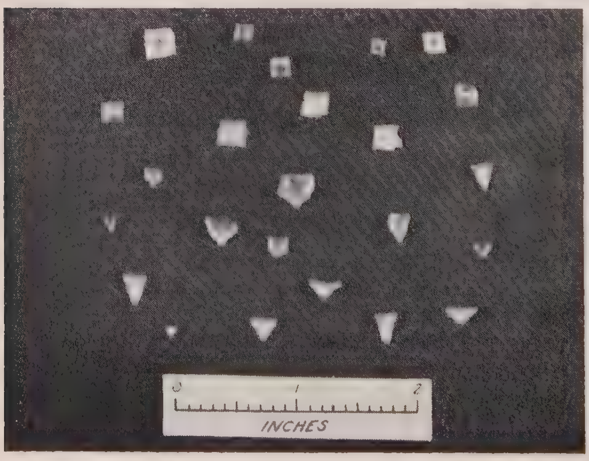

Fig. 1. Artificial hopper crystals.

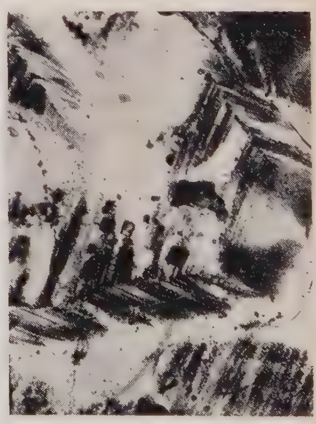

Fig. 2. Photomicrograph of hopper crystals outlined by oriented liquid inclusions. (×18)

Growth of salt crystals at the surface of present day saline lakes and basins is not uncommon and the hopper crystals have been reported by Eardley (1938) in the salt mush along the margins of Great Salt Lake.

This same type of crystal has been observed in the Salina salt near the base of the core of the G. Bradley No. 4 well in Newaygo County, Michigan. The crystals shown come from a depth of approximately 4900 feet. In general the thick salt beds occur as alternating layers of clear, coarsely crystalline salt and cloudy, finely crystalline salt. These layers may be interrupted or separated by tissue thin layers of anhydrite and/or dolomite. Petrographic examination has shown that the cloudy appearance of alternate layers is due to an abundance of brine inclusions in the form of negative crystals. These inclusions have a linear orientation and the intersection of two series of parallel lines produces a chevron structure. Chance orientation of several crystals has facilitated the identification of the hopper structure (Fig. 2). The darkened zones are caused by the inclusion banding. It is interesting to note that the artificial hopper crystals, as well as the natural ones, contain an abundance of negative crystals and there is at least a suggestion that these inclusions are in part a function of surface growth.

REFERENCES

EARDLEY, A. J. (1938), Sediments of Great Salt Lake, Utah: *Am. Assoc. Petroleum Geologists, Bull.*, **22,** 1305–1411.

MILLER, B. L. (1937), Casts of halite crystals in the Beekmantown limestone: *Pennsylvania Acad. Sci. Proc.*, **11,** 55–57.

The Midwest Inter-Library Center

An all-day meeting of geologists, representing 13 midwestern university geology departments, was held on February 28, 1953, at the Midwest Inter-Library Center in Chicago. The meeting was called by the Center to explore possiblities for the cooperative acquisition of less-used but important library materials in the field. As an outgrowth of the discussions, the geologists decided that the universities that participate in the Midwest Center might appropriately supplement their own collections with a comprehensive collection of foreign geologic maps and with files of minor and less-used journals, particularly those of foreign academies. Such materials would be acquired by and housed at the Center for the joint use of the several institutions.

The Center purchases less-used research books and periodicals that its individual member libraries cannot afford and extends the use of them freely within the group of participants. It was established in 1949 with a million-dollar foundation grant and is supported and controlled by 16 member universities. Its new library building in Chicago has bookstacks with a three-million-volume capacity and is connected with each member library by teletype.

The participants at the February 28 meeting in Chicago were:

Eugene N. Cameron (U. of Wisconsin).
Leland Horberg (U. of Chicago).
Arthur L. Howland (Northwestern U.).
Brian H. Mason (Indiana U.).
Archie J. MacAlpin (U. of Notre Dame).
R. C. Moore (U. of Kansas).
Willard H. Parsons (Wayne U.).
John L. Rich (U. of Cincinnati).
Charles H. Summerson (Ohio State U.).
George A. Thiel (U. of Minnesota).
James W. Trow (Michigan State Coll.).
Sherwood D. Tuttle (State U. of Iowa).
George W. White (U. of Illinois).

Library Consultants were:

Lyle E. Bamber (Natural History Librarian, U. of Illinois).
Leon Marshak (Research Staff, John Crerar Library).
George R. Meluch (Purdue U. Library).
Mrs. Marie K. Shaw (Science Librarian, Wayne U.).

Genesis of Clays and Related Minerals

This will be the theme of the *Clay Minerals Conference* to be held at the *University of Missouri, Columbia, Missouri, on 15-17 October, 1953*. The Conference is sponsored by the Clay Minerals Committee of the National Research Council. Anyone interested in presenting a paper on this theme or on clay mineralogy, technology, physical behavior of clays, techniques of mineral determination, origin of soils, clays in soils, origin and distribution of clays in soils, clays related to ore deposits, and allied topics, please write *Mr. A. F. Frederickson, Washington University, St. Louis, Missouri*. A detailed program, including field-trip information, will be available on request in August, 1953. Everyone interested in any aspect of clay mineralogy or technology is cordially invited to attend the Conference.

Symposium on Geochemistry

A symposium on geochemistry will be held in Zürich, Switzerland, August 10–15, 1953. *President:* Michael Fleischer; *Local Chairman:* C. Burri. The symposium will be held under the auspices of the Section of Inorganic Chemistry of the International Union of Chemistry and will be devoted to two general themes:

(1) The problem of organizing and making available geochemical data: Reports by organizations engaged in revision and compilation of existing data of geochemistry, compilation and computation of rock analyses, etc.

(2) Geochemical research the world over, with a summary of replies received to questionnaire, and individual reports on current work from various centers.

The scientific sessions will be followed by a one or two-day field excursion.

A complete program will be sent upon request. Apply to the secretary: *Prof. T. F. W. Barth, Geologisk Museum, Oslo 45, Norway.*

At a meeting held at Tokyo University on June 30, 1952, it was decided to establish The Mineralogical Society of Japan.

The following officers were elected:

President: Zyunpei Harada, Hokkaido University, Sapporo.
Secretaries: Toshio Sudo, Keiichi Omori.
Treasurer: Bumpei Yoshiki.
Editors: Nobuo Katayama (Chief); Zyunpei Harada, Jitsutaro Takubo, Toyofumi Yoshimura.

In addition a Council consisting of 16 members was selected. Two journals are contemplated, one "Kobutsugaku Zasshi (Mineralogical Journal) in Japanese, and "Bulletin of the Mineralogical Society of Japan" in foreign languages.

Nos. 1 and 2 of the Kobutsugaku Zasshi were published in Sept. 1952, and January 1953. Number 1 of the Bulletin is in preparation.

The National Academy of Sciences at its annual meeting in Washington elected 30 new members and two foreign associates. Among the new members elected were Martin J. Buerger, professor of mineralogy and crystallography at the Massachusetts Institute of Technology, and John F. Schairer, physical chemist at the Geophysical Laboratory, Washington, D. C.

To gauge interest in the proposed *Abstract Journal*, to plan size of editions and to estimate subscription price, it is urged that all who would be willing to pay not more than $2.00 for an annual subscription of four issues, to send a post card indicating your interest to *American Geological Institute, 2101 Constitution Ave., Washington 25, D. C.* (Send no money now).

MINERALOGICAL SOCIETY (LONDON)

A meeting of the Society was held on Thursday, January 22nd, 1953, at 5 P.M., in the apartments of the Geological Society of London, Burlington House, Piccadilly, W.1 (by kind permission).

The following papers were read:—

(1) CHERALITE, A NEW MINERAL OF THE MONAZITE GROUP.

By Mr. S. H. U. Bowie and Mr. J. E. T. Horne.

The name cheralite is proposed for a new mineral of the monazite group from a kaolinized pegmatite at Kuttakuzhi, 23 miles E.S.E. of Trivandrum, Travancore. The mineral, which is remarkable for its high contents of ThO_2 (31 50%), U_3O_8 (4.05%) and CaO (6.30%), has the formula (TR, Th, U, Ca) (P, Si) O_4, where TR is dominantly Ce, La, Pr and Nd.

It occurs as rough green crystals with the following physical properties: cleavage (010) distinct, (100) difficult, parting on (001) poor; hardness 5; specific gravity 5.28; $\alpha=1.779$, $\beta=1.780$ and $\gamma=1.816$; $2V_\gamma=18°$; $X=b$, $Z\wedge c$ 7°.

X-ray powder data show that cheralite is isostructural with monazite, huttonite and synthetic $CaTh(PO_4)_2$.

(2) CRICHTONITE, A DISTINCT SPECIES.

By Dr. F. A. Bannister, Dr. G. F. Claringbull and Dr. M. H. Hey.

Crichtonite described by de Bournon in 1813 and long supposed to be a variety of ilmenite has been shown to be a distinct species. It is rhombohedral with a very large unit cell having approximate dimensions $a=37$, $c=21$ Å, and has been shown to contain both ferric and ferrous iron with considerably more titania than ilmenite.

(3) *X*-RAY STUDIES OF BYTOWNITES AND ANORTHITES.

By Dr. P. Gay.

A number of bytownites and anorthites from different localities have been examined by *x*-ray methods. For almost pure anorthites two types of diffraction patterns may be distinguished: the presence of certain diffuse reflections may be used to differentiate between high and low temperature anorthites.

For patterns from less basic specimens it is probable that the presence of these reflections is influenced by the composition of the feldspar.

It is hoped that when the method is fully developed it will be of use to the petrographer in determining the previous geological history of basic plagioclases.

(4) THE ROLE OF WATER IN AMPHIBOLES.

By Dr. E. J. W. Whittaker.

Attention is drawn to the fact that the role of water in amphiboles in excess of that corresponding to two hydroxyl ions per formula unit can be inferred from the chemical analysis in certain cases. Two analyses of fibrous iron-bearing amphiboles are examined and shown to support the view that the excess water is present in the form of discrete molecules or extra hydroxyl ions, rather than as SiOH groups.

(5) PRELIMINARY *X*-RAY INVESTIGATIONS OF HILLEBRANDITE.

By Dr. L. Heller.

A single crystal of natural hillebrandite was investigated by *x*-ray methods. $a=16.60$, $b=7.26$, $c=11.85$ Å, $\alpha=\beta=\gamma=90°$. The *b* axis shows strong pseudohalving. The space group of the true structure is compatible with $P2_1/a$ (Z=12), and that of the pseudostructure with *Ccmm*, *Ccm*2 and *Cc*2*m* (Z=6). Difficulties arise in reconciling the cell content with the space-group of the pseudostructure.

The following papers were taken as read:—

(1) THE UNIT CELL AND SPACE GROUP OF CHLOR-SPODIOSITE (Ca_2ClPO_4).

By Dr. A. L. Mackay (Communicated by Dr. J. W. Jeffery).

Synthetic Ca_2ClPO_4, the chlorine analogue of the mineral spodiosite, was examined optically and by *x*-rays. Crystals are orthorhombic, with space group probably *Pbcm*, and dimensions $a=6.17$, $b=6.89$ and $c=10.74$ Å. Discrepancies in the literature are cleared up.

(2) THE PUMPELLYITE MINERAL SERIES.

By Dr. D. S. Coombs.

Pumpellyite from Calumet, Mich., has the following cell constants: $a=8.81\pm0.02$ Å, $b=5.94\pm0.01$ Å, $c=19.14\pm0.02$ Å, $\beta=97.6\pm0.2°$; space group $A2/m$. The *a* and *b* cell edges are closely similar to those of epidote and lawsonite, and oriented intergrowths of pumpellyite and lawsonite sharing these cell edges are described. The "basal cleavage" reported by various writers is ascribed to two different planes, there being a more easy cleavage parallel to (100) and a poorer cleavage parallel to (001). A thermal analysis by Dr. R. J. McLaughlin and powder photograph data are presented. Published chemical analyses are reviewed and are supplemented by semi-micro determinations of iron. These are used to draw up curves relating optical properties to iron content.

(3) A HYDROUS MICA FROM YORKSHIRE FIRECLAY.

By Mr. K. Carr, Dr. R. W. Grimshaw, and Professor A. L. Roberts.

A micaceous type mineral which was isolated from a Yorkshire fireclay has been shown by chemical, microscopic, *x*-ray and thermal tests to be an illite or hydrous mica. Flakes of the mineral, some of which are 2–3 mm. square, can be obtained in a very pure state. Along cracks and fissures there appears to be an alteration mineral which is most probably a kaolin type clay mineral. Structurally the hydrous mica can be ascribed to the recent notation of Norrish and Brown where oxonium ions are postulated as replacing alkali ions in the mica sheets.

The mineral appears to be diagenic in origin and a similar type is present, often in amounts up to 30%, in fireclays from many localities.

(*Titles and abstracts kindly submitted by G. F. Claringbull, General Secretary.*)

A meeting of the Society was held on Thursday, March 26th, 1953, at 5 P.M., in the apartments of the Geological Society of London, Burlington House, Piccadilly W.1 (by kind permission).

The following papers were read:—

(1) THE HYDRATED CALCIUM SILICATES RIVERSIDEITE, TOBERMORITE AND PLOMBIERITE.

By Mr. J. D. C. McConnell (communicated by Prof. C. E. Tilley).

The minerals riversideite, tobermorite and plombierite are shown to correspond to the three hydration states recognized in the calcium silicate hydrate (1) group by Taylor (1953). The characteristic (002) spacings are 9.6 Å, 11.3 Å and 14.6 Å respectively and the corresponding approximate molar water contents are 0.5, 1.0 and 2.5 mols. Tobermorite from Skye has been examined, and its variable refractive indices related to a variable water content. It consists mainly of the 11.3 Å hydrate.

The 11.3 Å hydrate, in a pure state, occurs in contact rocks at Ballycraigy, Larne, Northern Ireland. This mineral is orthorhombic $\alpha=1.570$, $\beta=1.571$ and $\gamma=1.575$; $a=\gamma$, $b=\beta$ and $c=\alpha$; $a=11.3$ Å, $b=7.33$ Å and $c=22.6$ Å; space group $C222$.

Both the 9.6 Å and 14.6 Å hydrates have been prepared from tobermorite from Ballycraigy. The 9.6 Å hydrate (artificial riversideite) has refractive indices $\alpha=1.600$, $\beta=1.601$ and $\gamma=1.605$. A natural material corresponding to the 14.6 Å hydrate is found at Ballycraigy and this has been identified with the mineral plombierite. Hydration of the minerals larnite and melilite is described.

(2) Natural and Synthetic Jalpaite (Ag_3CuS_2).

By Dr. G. F. Claringbull.

When investigating the silver-copper sulphides, G. M. Schwartz (1935) failed to synthesize or detect any mixed sulphide other than stromeyerite (AgCuS). Jalpaite (Breithaupt, 1858; Kalb and Bendig, 1924) is here confirmed by *x*-ray diffraction as a distinct phase in nature and has been synthesized from the melt. It has also been detected with acanthite in both natural and synthetic silver-copper sulphides containing as little as 5% Cu_2S.

The new evidence suggests that the low-temperature acanthite phase is stable only when relatively copper-free.

(3) A Granophyre from Coire Uaigneich, Isle of Skye, Containing Quartz Paramorphs After Tridymite.

By Prof. L. R. Wager, Mr. D. S. Weedon and Dr. E. A. Vincent.

The granophyre where examined to the S.E. of Blaven has a ring-dyke form, the margins being chilled against the country rock to a flinty material.

The chilled rocks contain 5% of phenocrysts, consisting of plagioclase (An_{50}), orthopyroxene (58% $MgSiO_3$) and tridymite, now inverted to quartz, set in a cryptocrystalline groundmass. The central part of the granophyre is shown to be derived from the same magma as the margin, both by chemical analysis and by the presence in each of similar phenocrysts in similar amount. In the central more coarsely crystalline part, the groundmass shows two different textures side by side; one characterized by a second generation of criss-crossing tridymite crystals and the other by areas of quartz and feldspar with a normal granophyric texture.

It is suggested that the granophyre was intruded at relatively high temperature, the marginal material being rapidly chilled to give a cryptocrystalline groundmass. Away from the margins the material cooled more gradually, allowing crystallization of a second generation of tridymite before the temperature fell sufficiently to permit normal granophyric intergrowth of quartz and feldspar. The two textures thus produced bear striking resemblances to those seen in certain thermally metamorphosed arkoses.

(4) Quantitative Mineralogical Analysis of Clay and Silt Fractions by Differential Thermal Analysis.

By Mr. R. J. McLaughlin.

The details of an apparatus for differential thermal analysis and its standardization are given. Clay and silt fractions from soil horizons of weathered arkoses are investigated using chemical, *x*-ray and differential thermal methods of analysis. The correlations between the three methods are discussed. It is shown that in the group investigated there is a direct relation between area of thermal peak and percentage of mineral present, and this may be used to obtain rapid quantitative evaluations. Effects of grain size, dilution of specimen and impurities are discussed in relation to their influences on the quantitative evaluation.

The following papers were taken as read:—

(1) High-order Plates for the Microscopic Examination of Mineral Grains.

By Dr. F. Smithson.

When the usual wedges or plates commonly employed for determining optical sign fail in cases of highly birefringent minerals, gypsum or quartz plates representing 10, 20 or 30 orders on Newton's scale are frequently effective. Preparation and use in determining sign of interference figure and sign of length are described.

(2) The Effect of Grinding on Micas: I. Muscovite.

By Dr. R. C. Mackenzie and Dr. Angela A. Milne.

Chemical, x-ray and thermal methods have been used to examine the changes induced by dry-grinding muscovite for periods up to 24 hours. The cation-exchange capacity increases with time of grinding up to about 150 m.e./100 g., and this figure can be approximately related to the amount of K^+ rendered exchangeable; the crystal structure appears to suffer almost complete breakdown after 8 hours, but a recrystallization occurs thereafter, the product differing from muscovite in several respects; an increase in hydration is shown by thermal measurements. After heating to 1000° C. the unground material is relatively unchanged but the ground material recrystallizes to leucite. These changes are correlated and discussed.

(3) The Relation Between Area and Volume in Micrometric Analysis.

By Dr. F. Chayes.

Discusses the theoretical basis of the micrometric analysis of rocks and in particular the superposition error (R. B. Elliott: *Min. Mag.*, **29**, 833).

(*Titles and abstracts kindly submitted by G. F. Claringbull, General Secretary.*)

BOOK REVIEWS

THERMOCHEMICAL METHODS IN SILICATE INVESTIGATIONS, By Wilhelm Eitel. x+132 pp., 63 figures. Rutgers University Press, New Brunswick, New Jersey. $4.75, 1952.

This little book, dedicated to the memory of Walter P. White, presents a meticulously documented review of the literature on methods and principles for thermochemical studies of silicates and related materials. The book evidently is an outgrowth of the author's chapter on "Thermochemistry of Silicates" in his extensive treatise, *Physikalische Chemie der Silikate* (Leipzig, 1941). The author explains in the preface that "many of the special methods described have their origin in European laboratories, but an attempt has been made to combine them with the methods of American investigators, especially Drs. Kelley and White."

The subject matter covered is evident from the chapter titles: Introduction, Heats of formation and reaction, Calorimeters for determination of heats of reaction, Thermochemical principles for the problem of reaction affinities, Experimental methods for determining reaction affinities, Examples for the calculation of free energy changes and affinities, and Possibility of anomalies at low temperatures; statistical meaning of entropy. There are two appendixes: one is on the evaluation of the results of water equivalent and heat of solution determinations; the other is on numerical data taken mainly from Dr. Kelley's publications and arranged in four tables—Heats of Formation, Data for Changes of State, Heat Capacity Equations, and Entropies. There is both a subject index and an index to compounds. References are presented at irregular intervals in the form of notes referring to numbers scattered throughout the text. There are 226 such notes in all.

In the first chapter after the Introduction, Dr. Eitel briefly discusses the need for special methods in silicate thermochemistry and explains why solution calorimetry is used predominantly in evaluating the heats of silicate reactions. This is followed by a chapter on calorimeters which first describes nearly all the solution calorimeters that have been developed to function satisfactorily. Dr. Eitel then discusses methods for determining heats of phase changes and the possibility of using the results of calibrated thermal analysis for this purpose. This chapter also contains a short discussion of the computation of heats of fusion from the melting curves in binary systems and takes up some of the errors inherent in the method in case of systems which depart from ideality. A section on the calculation of the heat of formation from structure energy and fundamental physical constants, mentioning advances made by Kapustinsky and other Russian workers, concludes the chapter.

The material dealing with reaction affinities reflects the author's long-standing interest in Nernst's theorem and its utilization for the calculation of the free energies of reaction from thermal data. The theoretical discussion proceeds along the orthodox lines developed by the Nernst school rather than along more modern lines. Third law is equated with Nernst's theorem and third law entropy is identified as absolute entropy.

In the chapter on experimental methods for determining reaction affinities are described the various calorimeters for measuring low and high temperature heat capacities, mentioning calorimeters developed in Europe as well as in this country, and including a brief discussion of calorimeters for the measurement of true heat capacities at high temperatures.

Many examples of results obtained in the calculation of free energy changes and reaction affinities for silicates from thermal data are included in the next to the last chapter. The examples quoted comprise most of the studies published on this subject in the field of silicates.

The last chapter deals with low temperature anomalies among which the author includes polymorphous transitions of second kind and the excess heat capacity of glasses over that of crystals. A very brief statement is given concerning the statistical meaning of entropy.

In Paragraph 21, the author mentions that tantalum presents certain advantages as material for the construction of a solution calorimeter for use with acids. It is not mentioned, however, that such a calorimeter could not be used with hydrofluoric acid solutions which corrode tantalum.

In a possible revised edition the reviewer would prefer to see a fundamental revision of the use of Nernst's theorem for the computation of reaction affinities. The Nernst theorem can not be said to be a strictly valid statement of the third law of thermodynamics. Such a revision would bring the treatment into accord with current practice in thermodynamic calculations and theory.

The book may be recommended as a useful manual for students wishing to familiarize themselves with the literature of the subject. It is well printed and attractively bound.

F. C. KRACEK,
Geophysical Laboratory, Washington, D. C.

GENETISCHE LAGERSTÄTTENGLIEDERUNG AUF GEOTEKTONISCHER GRUNDLAGE, by HANS SCHNEIDERHÖHN, E. Schweizerbart'sche Verlagsbuchhandlung (Erwin Nägele), Stuttgart, 1952; 42 pages, paper-bound. Price 6.00 DM.

This work on a geotectonic classification of ore-deposits is based upon a lecture before the Mineralogical and Geological Section of the Naturwissenschaftlichen Vereins für Kärnten in Klagenfurt on November 3, 1951, followed by a detailed discussion by many of the leading investigators of Alpine ore-deposits. It has already appeared in its entirety in the *Neues Jahrbuch für Mineralogie*, Nos. 2 and 3, 1952.

The hypothesis that Schneiderhöhn presents in this work is intended particularly to explain the Alpine type of ore-deposit, those that have no apparent "parentage" and do not fit well in the classifications of Lindgren or Niggli. The commonly accepted classifications of ore-deposits relate them to igneous intrusions and their emanations. This type of ore-deposit is recognized in Schneiderhöhn's new classification as the "magmatic sequence" and differs in no respect from classifications already accepted, but there are types of deposits that cannot be related to definite igneous intrusions, and these are the principal subjects of Schneiderhöhn's discourse.

One of the main points in Schneiderhöhn's hypothesis is that since Cambrian time there have been only one or two metallogenetic orogenies. In Eurasia the late Paleozoic Variscian orogeny is the parent of ore-deposits. All other European or Asiatic orogenies are sterile of juvenile metallization. In North America the Appalachian and Ouachitan Variscian orogeny is accompanied by relatively weak metallization, the principal metallogenetic orogeny being the Nevadan and its related Laramide orogenies.

If a metal-bearing orogen remains undisturbed, erosion eventually reveals its accompanying metallization in all its facies and their lateral and temporal transitions of pure magmatic type. But disturbance of an orogen may bring about a regeneration or redistribution of the metallization of the "Urorogen." The characteristics and classification of this new class "Regenerated Ore-deposits" are discussed in detail.

To the student of European ore-deposits, as well as the investigator of certain Asiatic areas (Japan, Indonesia, etc.), this hypothesis will have considerable interest. To the investigator of American ore-deposits, where the magmatic sequence is so well defined, there seems little opportunity to invoke this hypothesis. In the case of the "Tri-State" lead-zinc deposits a "regenerated" origin should be considered.

This small work of Schneiderhöhn's, while not entirely new, is formulated in precise terms, and should stimulate a renewed interest in some of the neglected phases of ore-deposit classification. A reappraisal of the role of magmatism in metallogenesis would be in order at this time. This discourse is an important contribution to such a reappraisal.

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INCLUSIONS AS A MEANS OF GEMSTONE IDENTIFICATION, by Edward J. Gueblin, ix+223 pp., 258 illustrations which include 66 plates (1 colored). Gemological Institute of America, Los Angeles, Calif., 1953. Price $6.75.

This profusely illustrated book by Dr. E. J. Gueblin of Luzerne, Switzerland, is the result of prolonged study of the inclusions in gemstones. It is indicated that inclusions are a very valuable means of identification and may also serve to establish the source of natural gemstones. Natural and synthetic gems are reliably distinguished by means of their inclusions.

There are 23 chapters, a selected bibliography, and a statement concerning the author. Solid and liquid inclusions, cracks and fissures as inclusions and those resulting from growth phenomena, as well as inclusions in synthetic stones, in reconstructed ruby, and in glass and assembled stones are discussed in eight chapters. The inclusions observed in 16 gem minerals are described in detail in 14 chapters. The minerals considered are diamond, ruby, sapphire, emerald, aquamarine, garnet, topaz, spinel, tourmaline, quartz, peridote, moonstone, andalusite, kyanite, zircon, and fluorspar. There is no index.

The numerous plates are an impressive feature of the book. In describing the characteristic features of inclusions the author frequently does so in terms which are not currently used by petrographers, such as, "hoses," "hose-like," "slabs," and "crumbs." Thus, "slabs of hematite" may occur as inclusions. There are numerous other cases. In addition, the text includes many expressions which could be simplified and markedly improved.

The book should, however, serve as a valuable aid in the study of mineral inclusions and their use in the identification of the gemstones discussed.

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